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VOLUME XXX

NUMBER THREE

# RUBBER CHEMISTRY AND TECHNOLOGY

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PUBLISHED IN FIVE ISSUES BY THE  
DIVISION OF RUBBER CHEMISTRY  
OF THE AMERICAN CHEMICAL SOCIETY





# KOSMOS 60

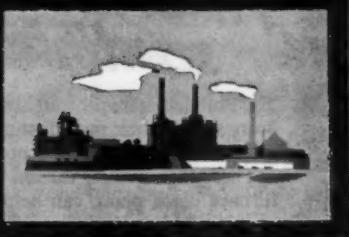
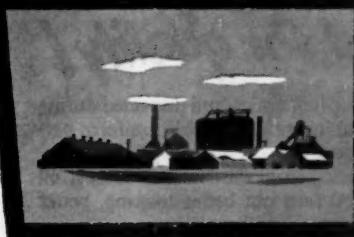
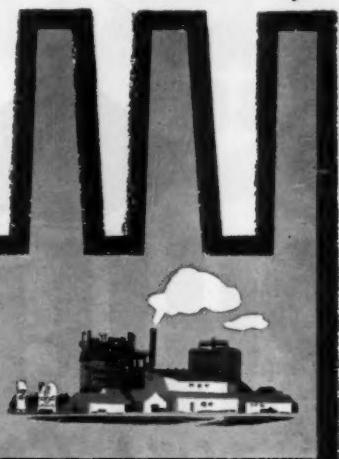
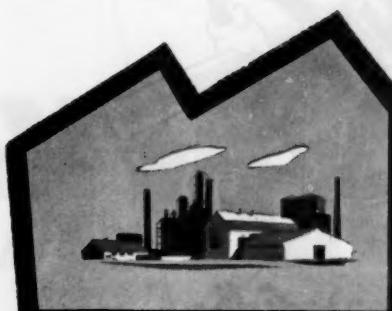
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Separate locations—yes...but the same high quality comes from all Witco-Continental plants. Produced under strict laboratory control, these rubber blacks are designed to meet all customer specifications.

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# COLORS

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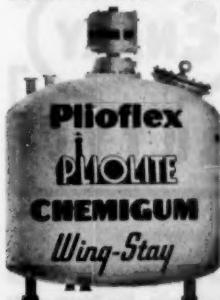
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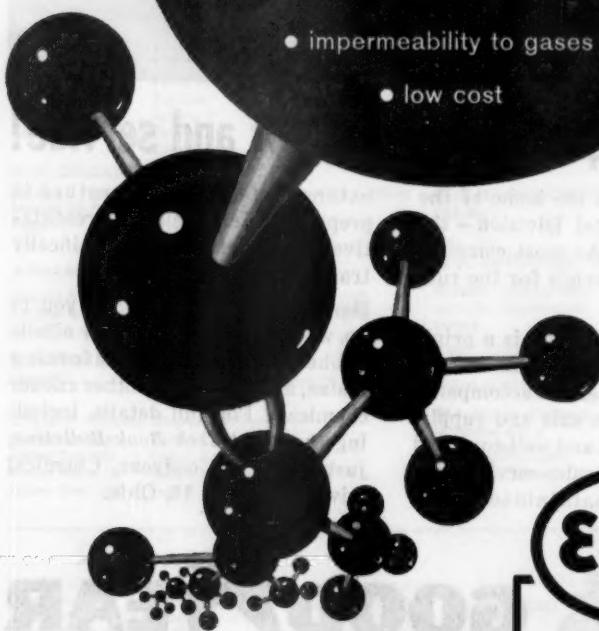
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- low cost



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Published by AMERICAN CYANAMID COMPANY, Rubber Chemicals Department, Bound Brook, New Jersey

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Free-flowing Antioxidant 2246 is soluble in most organic solvents. In the rubber itself, solubility at room temperature is somewhat greater than 2.0%. At recommended dosages, therefore, the possibility of bloom is remote. Antioxidant 2246 has good dry-storage stability, is non-toxic under normal conditions of use, and imparts no odor to the rubber stock.

The effectiveness of Antioxidant 2246 has been fully proved in applications ranging from drug sundries to footwear, from rubber thread to latex compounds. Full details on Antioxidant 2246 are given in Rubber Chemicals Technical Bulletin No. 815C.

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This antioxidant offers excellent protection against oxidation in natural rubber, SBR and neoprene. It is beneficial against fatigue caused by flexing, disperses readily in dry rubber, can be water-dispersed for latex compounds, and has little or no effect on scorching tendency or cure in the dosage recommended. Cured physical properties are satisfactory with commonly used accelerators. No odor is imparted to rubber stocks in which Antioxidant 425 is used.

This premium grade rubber chemical is a cream-to-white free-flowing powder with excellent storage stability. It is not toxic under normal conditions of use. Antioxidant 425 is soluble in acetone, benzene, gasoline and most other organic solvents . . . insoluble in water.

The chemical and physical properties, compounding activity and product uses of Antioxidant 425 are fully described in Rubber Chemicals Technical Bulletin No. 840.

For copies of these valuable additions to your bookshelf, contact your Cyanamid Rubber Chemicals Representative or write direct to American Cyanamid Company, Rubber Chemicals Department, Bound Brook, New Jersey.



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Try them and prove to your own satisfaction that they can give you better products for less money.



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Steadily increasing numbers of compounders are now using Hi-Sil 233, Columbia-Southern's white silica reinforcing pigment, in recipes that formerly called for either silicate type reinforcers or carbon blacks. Here are four reasons why:

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2. Much better physical properties at the same pound-volume cost.
3. Measurably equal quality at lower pound-volume cost.
4. In some instances, improved quality at slightly lower pound-volume cost.

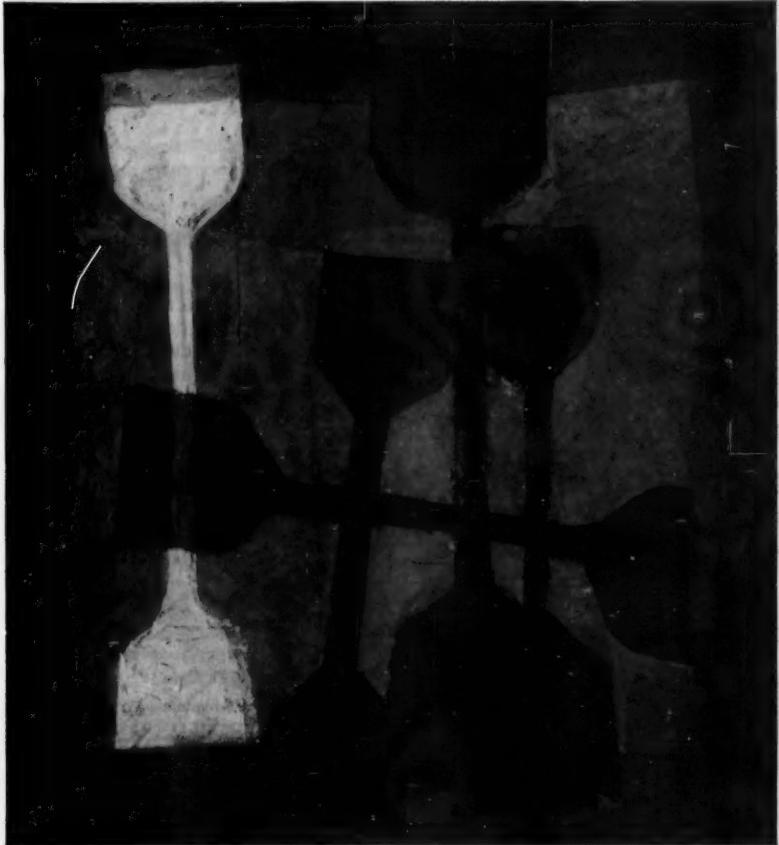
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# MONSANTO RUBBER CHEMICALS ANSWER A FREQUENTLY ASKED COMPOUNDING QUESTION

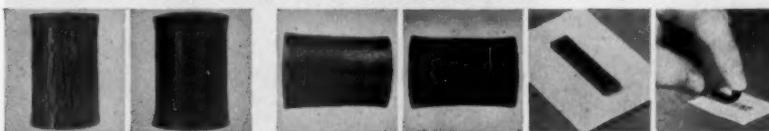
**QUESTION:** What new, solid antiozonant guards rubber against ozone cracking with minimum staining ???

**ANSWER :**

New Santoflex 6P

Monsanto announces Santoflex GP—the newest and best antiozonant you can use to "vaccinate" rubber against ozone attack. "GP" shows minimum staining. Now you can benefit from an antiozonant in mechanical goods and other industrial products just as tire-makers do in their compounds...Santoflex GP gives prolonged crack resistance to belting, electrical insulation, motor mounts, hose and appliance parts. An easily handled solid, "GP" imparts excellent ozone resistance.

**Static Ozone Test (48 Hours)**      **Dynamic Ozone Test (36,000 Fluxes—48 Hours)**      **Migration Stain Test**



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**SEND COUPON FOR SAMPLES...TECHNICAL HELP** Every application, plant and process has different compound requirements. That's why Monsanto recommends no "canned" formulations or "cure-alls"—we do offer samples of Santoflex GP along with technical help in testing it out for your specific application. The coupon is for your convenience.

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MONSANTO CHEMICAL COMPANY

Rubber Chemicals Department, Akron 11, Ohio

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# PHILPRENE

# PHILPRENE

*Use Philprene\* Rubber  
for non-staining qualities*

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	NON-PIGMENTED	PIGMENTED WITH PHILBLACK*
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	PHILPRENE 1001	PHILPRENE 1100 **
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	PHILPRENE 1500	PHILPRENE 1601
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<b>COLD OIL</b>	PHILPRENE 1503	
	PHILPRENE 1703	PHILPRENE 1803
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	PHILPRENE 1708	
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No stains from your soles! White tire walls will be white! Light-colored rubber goods including sponge, will be free from discoloration when you use the *right* Philprene rubber.

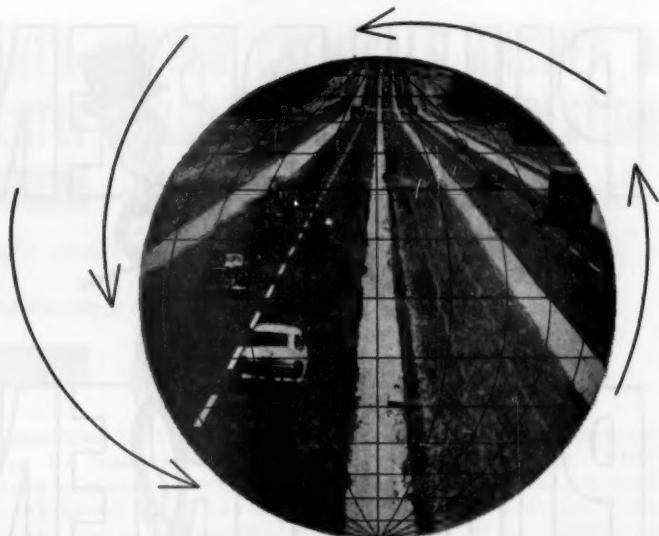
Philprene polymers are available in hot, cold, pigmented, non-pigmented and cold oil types, many of which are non-staining, with others designed for special applications.

Write for our Philprene Polymers brochure. There are many Philprene Polymers from which to choose. Consult your Phillips representative to determine which are best suited for your products. Phillips technical service and laboratory facilities can help solve your individual problems. Take full advantage of this service.

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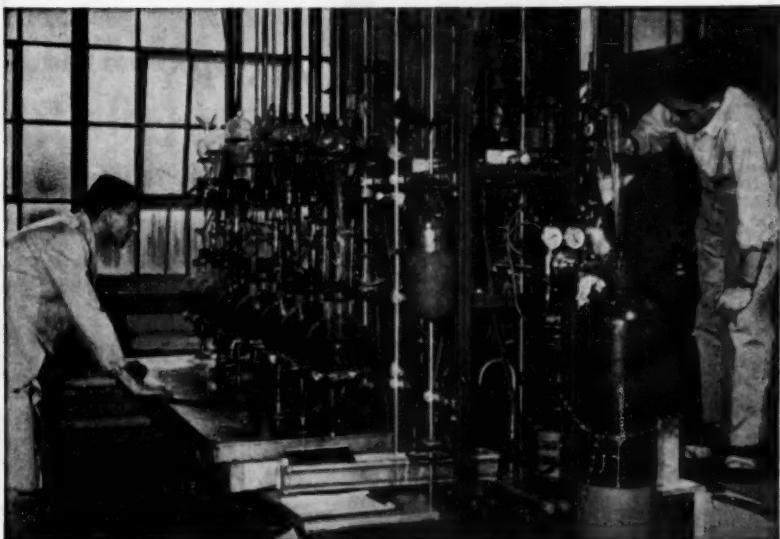


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JULY-SEPTEMBER • 1958

VOLUME XXXI

NUMBER THREE

# RUBBER CHEMISTRY AND TECHNOLOGY

PUBLISHED IN FIVE ISSUES BY THE  
DIVISION OF RUBBER CHEMISTRY  
OF THE AMERICAN CHEMICAL SOCIETY



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for RUBBER COMPOUNDING

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**STATEX®-125 ISAF**

(Intermediate Super Abrasion Furnace)

**STATEX-R HAF** (High Abrasion Furnace)

**STANDARD MICRONEX® MPC**

(Medium Processing Channel)

**MICRONEX W-6 EPC** (Easy Processing Channel)

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**STATEX-M FEF** (Fast Extruding Furnace)

**STATEX-93 HMF** (High Modulus Furnace)

**STATEX-G GPF** (General Purpose Furnace)

**FURNEX® SRF** (Semi-Reinforcing Furnace)

\* COLUMBIAN COLLOIDS \*

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380 Madison Ave.



New York 17, N.Y.

# RUBBER CHEMISTRY AND TECHNOLOGY

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July–September 1958

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## 73RD MEETING OF THE DIVISION OF RUBBER CHEMISTRY OF THE AMERICAN CHEMICAL SOCIETY, MAY 14-15-16, 1958, NETHERLANDS PLAZA HOTEL, CINCINNATI, OHIO

### TECHNICAL PROGRAM

#### URETHANE RUBBERS, LATEXES, ETC.

R. F. DUNBROOK, *Presiding*

1. Introductory Remarks, Chairman, R. F. DUNBROOK.
2. Chemistry of Aryl Isocyanates: Rate and Equilibrium Constants for the Formation and Decomposition of Ethyl, Diarylallophanates, I. C. KOGON, Elastomer Chemicals Dept., Jackson Laboratory, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.
3. Gelation and Viscosity Control in Isocyanate Reactions. R. P. KANE, I. C. KOGON, and H. W. BRADLEY, Elastomer Chemicals Dept., Jackson Laboratory, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.
4. Liquid Urethane Elastomers. R. J. ATHEY, Elastomer Chemicals Dept., Elastomers Laboratory, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.
5. Polyurethane Foams: Stability, Collapse, and Shrinkage. H. K. FRENSDORFF, Elastomer Chemicals Dept., Jackson Laboratory, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.
6. Effect of Swelling on Properties of Elastomers. C. B. GRIFFIS, A. WILSON, and J. C. MONTERMOSO, Quartermaster Res. and Dev., U. S. Army, Natick, Mass.

7. The St. Joe Ozone Flex Tester for Rubber Compounds. L. E. CARLSON and R. S. HAVENHILL, St. Joseph Lead Co., Monaca, Penna.
8. The Influence of Particle Size on the Viscosity of Synthetic Latex. Effect of Polydispersity. P. H. JOHNSON and R. H. KELSEY, Firestone Tire and Rubber Co., Akron 17, Ohio.
9. The Influence of Particle Size on the Viscosity of Synthetic Latex. The Effect of Particle Spacing. R. H. KELSEY and P. H. JOHNSON, Firestone Tire and Rubber Co., Akron 17, Ohio.  
High Speed Photography in the Rubber Industry. F. S. CONANT et. al., Firestone Tire and Rubber Co., Akron 17, Ohio.

#### SYMPORIUM ON HIGH TEMPERATURE RESISTANT ELASTOMERS. I.

##### Invited Papers

E. R. BARTHOLOMEW, *Presiding*

10. Introductory Remarks, Symposium Chairman, E. R. BARTHOLOMEW.
  11. Properties of Elastomers up to 500° F. F. M. SMITH, Firestone Tire and Rubber Co., Akron 17, Ohio.
  12. Viton—Heat and Fluid Resistant Elastomer. W. V. FREED, Elastomer Chemicals Dept., Elastomers Laboratory, E. I. du Pont de Nemours and Co., Inc., Wilmington, Del.
  13. Combined Effects of Heat and Gamma Radiation on Practical Rubber Compounds. E. E. MOONEY, S. T. SEMEGEN, and J. W. Born, The B. F. Goodrich Research Center, Brecksville, Ohio.
  14. Behavior of Some Elastomers in Petroleum Base Fuel at Elevated Temperatures. R. G. SPAIN, Wyandotte Chemicals Corp., Wyandotte, Michigan.
  15. The Vulcanization of Butyl Rubber with Phenol Formaldehyde Derivatives. P. O. TAWNEY, J. R. LITTLE, and P. VIOHL, United States Rubber Co., Res. Center, Wayne, N. J.
  16. High Temperature Resistance of Bonded Polymer to Metal Assemblies (400-450° F.). S. L. BRAMS and F. W. GAGE, Dayton Chemical Products Lab., Inc., West Alexandria, Ohio.
- Business Meeting—Best Paper Award to H. E. DIEM, H. TUCKER, and C. F. GIBBS, The B. F. Goodrich Research Center, Brecksville, Ohio.

#### SYMPORIUM ON HIGH TEMPERATURE RESISTANT ELASTOMERS. II.

##### Contributed Papers

E. H. CUNNINGHAM, *Presiding*

17. A New Chlorine-Containing Elastomer. L. T. EBY and J. V. Fusco, Enjay Company, Inc., Elizabeth, N. J.

18. Natural Rubber Compounds for High Temperature Service in Air. W. P. FLETCHER and S. G. FOGG, British Rubber Producers' Research Assoc. Herts, England.
19. Inflatable Seals for High Temperature Service. M. A. NADLER, D. ALKIRE, W. A. CARR, and F. J. FRENCH, North American Aviation, Inc., Downey, Calif.
20. Melting and Glass Transitions in Polyisobutylene. R. M. KELL, B. BENNETT, and P. B. STICKENY, Battelle Memorial Institute, Columbus, O.
21. Behavior of Silicone Rubber in Sealed Systems at High Temperatures. W. J. BOBEAR, General Electric Co., Chemical and Metallurgical Div., Waterford, N. Y.

#### General Papers

22. Compression Set of Silicone Rubber. C. W. ROUSCH and S. A. BRALEY, JR., Dow Corning Corp., Midland, Mich.
23. Polymer Composition Versus Low Temperature Characteristics of Polysiloxane Elastomers. K. E. POLMANTEER and M. J. HUNTER, Dow Chemical Corp., Midland, Mich.

### VULCANIZATION AND REINFORCEMENT

S. C. NICOL, *Presiding*

24. Pore Sizes and Pore Size Distribution in Reinforcement Pigment Particles. A. VOET, J. M. Huber Corp., Borger, Texas.
25. Influence of Carbon Black and Loading on Temperature-Retraction Properties of Elastomeric Compounds. F. W. BARLOW and R. W. CRETNEY, Thermatomic Carbon Co., Sterlington, La.
26. Odd Electrons in Rubber Reinforcing Carbon Blacks. G. KRAUS and R. L. COLLINS, Phillips Petroleum Co., Bartlesville, Okla.
27. A Theoretical Treatment of Elastomer Rupture. LAURA E. CASE and L. C. CASE, Purdue Univ., Lafayette, Ind.
28. Direct Determination of Combined Sulfur in Rubber Vulcanizates. W. J. DERMODY, The Electric Storage Battery Co., Philadelphia, Penna.
29. The Temperature Coefficient of Vulcanization of Butyl Rubber. J. G. MARTIN, and R. F. NEU, Enjay Laboratories, Linden, N. J.
30. Vulcanization of Elastomers by Electron Beam Irradiation. H. A. WINKELMANN, Dryden Rubber Div., Sheller Mfg. Corp., Chicago, Ill.
31. Chemical Loaded Molecular Sieves as Latent Curing Aids. I. Secondary Accelerators in Styrene-Butadiene Rubber. F. M. O'CONNOR, T. L. THOMAS, and M. L. DUNHAM, Union Carbide Corp., Tonawanda Lab., Tonawanda, N. Y.

## FUTURE MEETINGS

Meeting		City	Hotel	Date
1958	Fall	Chicago	Sherman	September 10-12
1959	Spring	Los Angeles	Biltmore	May 12-15
1959	Fall	Washington*	Shoreham	November 9-13
1960	Spring	Buffalo	Statler	May 24-27
1960	Fall	New York	Commodore	September 13-16
1961	Spring	Louisville	Brown	May 16-19
1961	Fall	Chicago	Sherman	September 5-8
1962	Spring	Boston	Statler	May 15-18

\* An international meeting jointly sponsored by the Division of Rubber Chemistry ACS, Committee D-11 of ASTM, and the Rubber and Plastics Division of ASME.

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#### 1958

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# AERATION OF NATURAL RUBBER LATEX. I. EFFECT OF POLYAMINES ON THE HARDNESS AND AGING CHARACTERISTICS OF AERATED LATEX RUBBER \*

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## INTRODUCTION

It is generally accepted that many of the changes in the physical properties of natural rubber when exposed to air or oxygen are due to changes in the molecular weight of the rubber, i.e., to chain scission or to crosslinking reactions, the mechanisms of which are still not fully understood. At elevated temperatures and in the presence of not too small a partial pressure of oxygen, oxidative scission of the rubber normally predominates over crosslinking, while the reverse is often true at ambient temperatures. Thus, crosslinking reactions normally occur in sheet rubber on storage<sup>1,2</sup>, as shown by an increase in the gel content and hardness of the rubber. Messenger<sup>3</sup> and Wood<sup>4</sup> both found that moisture tended to inhibit the hardening effect; Gale<sup>5</sup> confirmed their results and also reported that rubber dried under humid conditions was more susceptible to subsequent breakdown at elevated temperatures. In latex systems, Bevilacqua<sup>6</sup> showed that harder rubbers were obtained from ammoniated latexes, after storage, than from latexes preserved with aliphatic amines or formaldehyde. Philpott<sup>7</sup> found that the hardening of rubber could be accelerated by the addition of benzidine hydrochloride to latex prior to coagulation, and similar results were obtained by Bloomfield<sup>8</sup> even when oxygen was rigorously excluded from the system. The latter author also showed that acetone extraction of rubber resulted in considerable hardening without any apparent structural changes since the original plasticity of the rubber could be restored by re-incorporating the acetone extract. Recently Wren<sup>9</sup>, who developed techniques of aerating latex under controlled conditions in these laboratories, found that latexes on prolonged aeration gave rubbers which were soft and degraded. In the present work an investigation has been made of the influence of various polyfunctional amines on the hardness and aging characteristics of ordinary and aerated latex rubber.

## RESULTS

Table I shows the effect of adding tetraethylenepentamine (TEP) to ammoniated latex 30 minutes prior to coagulation and creping. The crepes were dried at room temperature (30° C) and Mooney viscosity and Williams plasticity figures determined. Plasticity measurements were made before and *after air oven aging* the samples at 100° C. The increase in viscosity and in the recovery figures in the unaged plasticity measurements indicate increased cross-

\* An original publication.

linking of the rubber in the presence of TEP; the improved aging behavior of the samples containing TEP is also apparent.

Similar results have been obtained with other polyfunctional amines, including benzidine. In Table II Williams plasticity values are shown for dried films of a latex to which 0.5% (on the weight of rubber) of different amines had been added.

*Effect of aeration.*—To determine the effect of aeration of the latex on the hardness and aging behavior of the rubber, samples of an ammoniated latex in

TABLE I  
EFFECT OF TEP ON THE VISCOSITY AND PLASTICITY OF CREPE RUBBER

Additive, % by wt. on rubber	Mooney viscosity	Williams plasticity (M.MS)					
		Unaged		After 24 hrs at 100° C		After 48 hrs at 100° C	
		D <sub>10</sub>	Rec. in mm	D <sub>10</sub>	Rec. in mm	D <sub>10</sub>	Rec. in mm
— (control)	75	4.4	5.7	2.5	3.1	1.3	1.4
0.5 TEP	87	4.6	5.8	4.0	7.4	2.8	4.2
1.0 TEP	90	5.1	7.0	4.9	9.8	4.5	9.8

half-filled containers were slowly rotated on a roller mill for periods up to 172 hours. The oxygen absorbed was replenished by opening the containers once every 24 hours. Dried films of the latexes were then tested for Mooney viscosity, intrinsic viscosity, gel content and plasticity before and after heating at 100° C. Similar measurements were carried out on films of the aerated latexes to which 0.5% of TEP was added 30 minutes before preparation of the films. Results are given in Table III. In the absence of TEP, the changes in intrinsic viscosity and plasticity point to increasing breakdown of the rubber with increase in the time of aeration but some crosslinking also occurs, as shown by the changes in gel content. Subsequent oxidative degradation at 100° C is ac-

TABLE II  
EFFECT OF AMINES ON THE PLASTICITY OF A LATEX FILM

Additive (0.5%)	Williams plasticity (M.MS)			
	Normal		48 hrs at 100° C	
None	4.4	7.9	2.9	5.2
TEP	4.3	6.9	4.2	9.3
Triethylenetetramine	4.3	7.0	4.0	8.7
m-phenylenediamine	7.0	12.5	5.2	12.0
Hydrazine	4.3	8.3	3.4	6.7
Benzidine	5.9	12.2	4.8	9.9

celerated by the aeration treatment. The most obvious consequence of adding TEP to the aerated latexes is to increase the percentage of gel rubber and decrease oxidative breakdown at 100° C.

*Storage of aerated latexes.*—In view of Bevilacqua's findings<sup>6</sup> that hardening of the rubber occurs during storage of ammonia-preserved latex, it was of interest to know whether a similar phenomenon took place on storing ammoniated latexes which had been deliberately exposed to oxygen by aeration. An

ammoniated latex was therefore aerated for 172 hours, as described above, after which portions were stored at room temperature in full containers for periods up to four weeks. Mooney viscosity and plasticity measurements on dried films of the samples are summarized in Table IV. The results of Table IV indicate clearly that not only does crosslinking of the rubber occur during storage of

TABLE III  
EFFECT OF AERATION AND TEP ON VISCOSITY AND PLASTICITY OF LATEX FILMS

Latex sample	Mooney viscosity	Intrinsic viscosity of sol fraction	Gel, %	Williams plasticity (M.MS)							
				Normal		24 hrs at 100° C		48 hrs at 100° C		D <sub>10</sub>	Rec.
				D <sub>10</sub>	Rec.	D <sub>10</sub>	Rec.	D <sub>10</sub>	Rec.		
1. Control, no aeration	78	8.6	2	4.8	6.8	3.7	5.5	3.6	5.2		
2. As (1) followed by 0.5% TEP	80	—	4	4.8	6.8	3.7	5.5	3.7	5.5		
3. 14 hrs aeration	82	7.6	15	4.3	6.0	3.4	5.0	1.8	1.9		
4. As (3) followed by 0.5% TEP	85	—	23	4.1	6.0	3.4	7.7	2.0	3.1		
5. 48 hrs aeration	80	6.0	18	3.9	5.9	3.1	4.5	Liquid			
6. As (5) followed by 0.5% TEP	84	—	31	3.8	6.6	4.2	7.3	3.9	6.4		
7. 172 hrs aeration	69	4.1	18	3.2	4.3	2.5	3.2	Liquid			
8. As (7) followed by 0.5% TEP	75	—	40	3.3	5.2	4.1	8.7	3.9	6.6		

aerated latex, but that the aging characteristics of the rubber show a considerable improvement as a result of storage.

*Effect of aeration and of amines on storage hardening of rubber.*—Table V shows that in an accelerated storage test of dried rubber films at a temperature below that at which degradative reactions predominate, exposure of latex to air prior to coagulation and conversion into sheet markedly increases the tendency of the rubber to harden. The addition of TEP to such an aerated latex effectively prevents such hardening, although its effect in more prolonged storage tests at room temperature has yet to be determined. Benzidine has already

TABLE IV  
EFFECT OF TIME OF STORAGE OF AERATED LATEX ON VISCOSITY AND PLASTICITY OF DRY FILMS

Storage period, weeks	Mooney viscosity	Williams plasticity							
		Unaged		48 hours at 100° C				Oxidized	(Liquid)
		D <sub>10</sub>	Rec.	D <sub>10</sub>	Rec.	D <sub>10</sub>	Rec.		
Nil	80	4.0	5.5						
1	101	4.4	8.1	2.7	4.2				
2	104	4.0	7.1	2.6	6.3				
3	106	4.7	8.2	3.9	8.2				
4	108	4.6	8.8	4.1	8.2				

been proved effective in this role in storage tests extending up to 12 months at Malayan and European temperatures<sup>10</sup>.

#### DISCUSSION

Explanations previously advanced for the hardening of rubber during storage fall into three groups. The first attributes changes in hardness to variations in the nonrubber constituents, and was first proposed by de Vries<sup>1</sup>. Under

certain conditions, the slow decomposition of some of the nonrubber constituents may well influence to some extent the hardness of the rubber, as might be expected from Bloomfield's experiments on acetone-extracted rubber. The second view, proposed by Wood<sup>4</sup>, is that storage hardening is due to a crosslinking of the rubber which may be initiated and maintained by the presence of peroxide or similar free-radical forming groups in the rubber. Thirdly it has been suggested<sup>11</sup> that abnormally weak links may be present in the natural polyisoprene chain which, by rupture, give rise to free radicals which may then react further to produce crosslinking and gelation of the rubber. It is, however, difficult to reconcile the last two proposals with the known ineffectiveness of additives such as hydroquinone, phenyl-2-naphthylamine, 2,2'-dithiobisbenzamidodiphenyl disulfide, xylol mercaptan and 2,4-dinitrophenyl benzothiazolyl sulfide in preventing storage hardening<sup>4</sup>. Moreover, dry storage can cause gel formation not only in natural rubber but in some synthetic rubbers, particularly when the polymer is derived fully or partly from diene type monomers, indicating that gelation in these cases, at least, must be accounted for in terms of the normal reactivity of unsaturated carbon compounds.

The results described in this paper are consistent with Wood's hypothesis that storage hardening is initiated by free-radical forming groups in the rubber.

TABLE V

Treatment of latex	Mooney viscosity of rubber	Mooney viscosity after 24 hrs at 60° C	% increase
None	65	70	8
Aerated for 170 hrs	48	94	92
Aerated for 170 hrs then 2% TEP added	64	71	11

The assumption that these groups are peroxidic in nature is difficult to confirm unequivocally. Latex contains reducing agents which invalidate determinations of peroxidic oxygen by conventional methods. Freshly prepared smoked sheet, however, is known to contain peroxidic oxygen—usually 10–30 ppm, though values as high as 100–150 ppm have been found in samples from packing houses and smallholdings. The fact that polyamines such as TEP promote the gelation of natural rubber (Table I) is further evidence for the peroxidic function of the groups responsible for gelation, since polyamines are well known activators for the hydroperoxide initiation of vinyl polymerizations. Such crosslinking by polyamines can in fact be greatly enhanced if both hydroperoxide and polyamine are added to latex<sup>12</sup>. It is well established that the autoxidation of rubber involves the formation of rubber hydroperoxides, and the results of Table III, in which aeration of the latex causes not only break down of the rubber but significant increase in the gel content, are difficult to explain except by the thesis that peroxidic groups in the rubber are the centers at which crosslinking occurs. Significantly, a very marked tendency to spontaneous crosslinking has been observed in hydroperoxy-terminated polybutadiene<sup>13</sup>. Finally, in part II of this paper it will be shown that graft polymerization between methyl methacrylate and natural rubber, which is normally initiated in our laboratories by TEP and cumene hydroperoxide, can be initiated effectively by TEP alone provided the rubber (latex) has first been aerated. In such sys-

tems it is concluded that rubber hydroperoxides are formed which take the place of cumene hydroperoxide in the initiation of polymerization.

It is clear from the present and earlier work that oxidative scission and cross-linking of the rubber, on storage, are competitive reactions whose relative importance is determined by temperature, humidity, availability of oxygen and probably several other factors. Among these is the presence of reducing agents in natural latex which resemble TEP in their ability to promote crosslinking of the rubber and enhance its aging behavior at elevated temperatures. Patent applications concerning certain aspects of this work have been filed and are pending.

#### ACKNOWLEDGMENTS

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#### SUMMARY

Evidence has been presented to support the hypothesis that the absorption of oxygen by ammoniated latex at room temperatures creates reactive groups on the rubber hydrocarbon. These reactive groups impart to the rubber peroxidic properties. Such peroxidic group formation is responsible for the breakdown and build up of rubber under different conditions of storage. Suitable reducing systems, particularly the alkyne polyamines crosslink rubber in latex and enhance the aging properties of rubber.

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## AERATION OF NATURAL RUBBER LATEX. II. GRAFT POLYMERIZATION OF VINYL MONOMERS WITH AERATED LATEX RUBBER \*

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### INTRODUCTION

In the preceding paper, the effect of aeration of ammoniated latex on the viscosity, plasticity and gel content of the rubber were described. It was concluded that peroxidic groups were introduced into the rubber, thereby increasing its susceptibility to molecular scission and crosslinking reactions. Addition of polyamines such as tetraethylenepentamine (TEP) was shown to promote crosslinking and gelation of the rubber, and to reduce oxidative degradation. Reference was also made to experiments, carried out in these laboratories, showing that aerated natural latex reacted readily with methyl methacrylate, in the presence of TEP, to form graft polymers. The object of the present work was to investigate the nature and locus of this graft polymerization reaction and the properties of the graft polymers so produced.

### EXPERIMENTAL METHODS

Aeration of latex was carried out by half filling porcelain jars with latex and rotating them on rollers for different periods of time. The oxygen absorbed was replenished daily by opening the jars for 5 minutes. All natural latexes used were preserved with 0.7% ammonia.

The efficiency of the aerated latexes in promoting the polymerization of methyl methacrylate was assessed as follows:

To aerated latex containing 20 g of rubber 20 g of methyl methacrylate were added, followed by 0.2 ml of 1% ferrous sulfate solution and 2 ml of 10% tetraethylenepentamine solution (aqueous). Reaction was then allowed to proceed for (usually) 18 hours, after which the total solids content was determined. In most experiments, the maximum temperature attained during the reaction was also noted.

The percentages of free rubber and free polymethyl methacrylate in the reaction product were determined by extraction with petroleum ether (b.p. 50–60° C) and acetone, respectively, allowing static diffusion of the solvents. The graft polymer content was then determined by difference. The molecular weight of the grafted polymethyl methacrylate was determined by the *tert*-butyl hydroperoxide degradation method as modified by McSweeney<sup>1</sup>.

### RESULTS

Table I shows the efficiency of different latex samples in promoting polymerization of methyl methacrylate. Samples 1, 2 and 3 were obtained from

\* An original publication.

the same (freshly prepared) field latex; sample 4 was an older, once-centrifuged latex concentrate. The first three samples were stored in half-filled containers for periods up to 30 days prior to reaction with the methacrylate.

Although the most reactive systems are produced by aeration of the latex, Table I shows that storage in the presence of air also tends to increase polymerization efficiency. We shall therefore use the general term "hydroperoxidized

TABLE I  
EFFECT OF STORAGE AND AERATION ON THE POLYMERIZATION  
EFFICIENCY OF DIFFERENT LATEXES

Sample	No storage		4 days storage		10 days storage		30 days storage	
	Temp. rise	% monomer polymerized	Temp. rise	% monomer polymerized	Temp. rise	% monomer polymerized	Temp. rise	% monomer polymerized
Field latex	Nil	0	2° C	25	2° C	20	2° C	30
Latex concentrate	2° C	15	2° C	16	2° C	24	4° C	40
Recentrifuged latex concen- trate	6° C	40	8° C	40	8° C	44	10° C	62
Centrifuged con- centrate aerated for 172 hours	41° C	84						

latexes" to describe systems which have been activated by contact with air either by storage, aeration or similar methods. The increase in reactivity obtained by recentrifuging the latex (sample 3) suggests that some of the non-rubber constituents act as polymerization inhibitors.

*Location of reactivity in hydroperoxidized latexes.*—The polymerization reactivity of the above latexes could be associated either with the polyisoprene or with some nonrubber substance in the latex. Although the results presented in Part I of this paper indicate clearly that the reactivity is associated with the rubber hydrocarbon, an examination of the two main fractions of latex (i.e., rubber and serum) individually was considered desirable. This was carried out either by ultracentrifugation<sup>2</sup>, or by creaming latex which had been aerated for 172 hours. Creaming was effected with ammonium alginate after addition

TABLE II  
POLYMERIZATION EFFICIENCY OF AERATED LATEX FRACTIONS

Sample	Temperature rise	% monomer polymerized
172 hours aerated latex	34° C	86
Ultracentrifuged cream	13° C	80
Ultracentrifuged serum	0° C	0
Creamed—cream	22° C	84
Creamed—serum	0° C	0

to the latex of 1% of ammonium oleate, on the weight of rubber. The ultracentrifugation was carried out at a speed of 20,000 rpm. In both cases only the rubber fraction was capable of initiating polymerization of methyl methacrylate (Table II).

*Influence of time of aeration.*—Three samples of the same ammonia-preserved latex concentrate were aerated for 14, 48 and 172 hours, respectively. The samples were then reacted with methyl methacrylate as described in the experimental section, except that 2.0 ml instead of 0.2 ml of a 1% aqueous solution of

ferrous sulfate were used per 100 g of methyl methacrylate. The reaction product was then creped, dried and analyzed (Table III).

With all three samples in Table III, it will be noted that the molecular weight of the grafted polymethyl methacrylate side chains is large and the percentage of polymerized methyl methacrylate present as free polymer is small. By contrast, if polymerization is initiated by salts of peracids or by activated

TABLE III  
EFFECT OF TIME OF AERATION ON REACTION BETWEEN  
RUBBER AND METHYL METHACRYLATE

Latex sample	Total poly-methyl meth-acrylate content of product, %	% free rubber	% free polymer	% graft material	Approximate mol. wt. of side chains
Aerated for 14 hours	43.7	22.6	3.3	74.1	725,000
Aerated for 48 hours	44.2	16.5	4.3	79.2	685,000
Aerated for 172 hours	49.0	13.8	6.8	80	585,000

hydroperoxides as described in previous publications<sup>8-11</sup>, a much larger percentage of the polymerized methyl methacrylate is present as free polymer. This difference is not influenced appreciably by the particular reducing agents (ferrous ion and tetraethylenepentamine) employed in the above experiments<sup>12-14</sup>. Similar results to those in Table III have been obtained using as the reducing system ferrous ion, glucose and sodium pyrophosphate or ferrous ion, hydrazine sulfate and ethylenediamine tetra-acetic acid.

The contrast between graft polymers prepared by the procedure described above and the products obtained by using peracid salts or activated hydroperoxides as catalysts extends to many of the physical properties of the polymers. These properties will be described in more detail in subsequent publications, but it should be mentioned that the wet gel strength of rubber-methyl methacrylate graft polymer latex coagulum is much higher when polymerization is promoted

TABLE IV  
POLYMERIZATION OF MONOMERS USING HYDROPEROXIDIZED LATEX

Monomer	Increase in temperature, °C	% monomer polymerized
Styrene	7	84
Methacrylic acid	12	89
Isobutyl methacrylate	15	89
Acrylonitrile	5	55
Ethyl acrylate	6	83
Methyl methacrylate	47	94

by aeration than when hydroperoxide catalysts are used as described by previous workers. The increased wet gel strength is accompanied by a greatly reduced tendency of the latex to form discontinuous, cracked films on drying. These properties of high wet gel strength and good film-forming characteristics are of prime importance in many latex applications.

*Polymerization of other vinyl monomers.*—Vinyl monomers other than methyl methacrylate which we have succeeded in graft polymerizing with natural rubber, using hydroperoxidized latex prepared by aeration, include methacrylic

acid, styrene, ethyl acrylate, isobutyl methacrylate and acrylonitrile. With acrylonitrile, methacrylic acid and styrene the concentration of TEP and ferrous sulfate necessary to obtain a substantial conversion of monomer after 18 hours reaction was twice that employed above. The percentage polymerization of different monomers, when reacted with an equal weight of rubber in the form of ammoniated latex concentrate which had been aerated for 172 hours, is shown in Table IV.

*Polymerization of mixed monomers in rubber latex.*—Suitable mixed monomers, e.g., methyl methacrylate and styrene, can be graft polymerized in natural rubber latex using cumene hydroperoxide, TEP and ferrous ion as the polymerization initiator. In the resulting product however, a considerable proportion (ca. 50%) of the polymerized monomers are present as free polymer. Furthermore, experience in this laboratory is that the over-all yield of product is liable to vary appreciably as the proportion of styrene to methyl methacrylate is varied. Table V shows the results obtained by the interaction of an ammoniated latex concentrate, aerated for 72 hours, with mixtures of styrene and methyl methacrylate in different proportions. In every case, a total of 50 g of monomer were reacted with 50 g of rubber, using TEP and ferrous ion as catalyst as described previously in this paper. The figures in Table V to be noted

TABLE V  
ANALYSIS OF COPOLYMER GRAFTS

Methyl methacrylate	Styrene	% yield of product	% free rubber in product	% free polymer in product
50	0	91	11.4	8.9
40	10	90	15.4	6.8
35	15	93	12.8	4.1
30	20	94	12.0	3.2
20	30	92	14.0	2.4
10	40	96	13.4	2.2
0	50	92	13.4	2.0

particularly are the low contents of free rubber and free polymer in the reaction product and the fairly small differences only in the over-all yield of product.

*Hydroperoxidation of synthetic latexes.*—As might be expected from the above work with natural latex, some synthetic rubbers produced wholly or in part from diene type monomers can be hydroperoxidized by a similar aeration procedure to that described above, although the time of aeration required to achieve reactivities comparable to those obtained with natural latex is usually considerably longer. A study of such systems and further work on the hydroperoxidation of natural latex is in progress.

#### DISCUSSION

The mechanism of the polymerization of methyl methacrylate, initiated by benzoyl peroxide or azoisobutyronitrile in the presence of natural rubber, has been studied in some detail. Using benzoyl peroxide as initiator, approximately one-half of the polymerized methacrylate is bound to the rubber as a graft polymer while the other half is present as free polymer, whereas with azoisobutyronitrile as initiator nearly all the polymerized methacrylate is in the form of free polymer. It has been established by Allen, Ayrey and Moore<sup>18</sup> that the formation of graft polymer is due to interaction between rubber hydro-

carbon and radicals derived from benzoyl peroxide, whereby free radical sites are produced in the rubber hydrocarbon, from which polymethyl methacrylate chains can grow. No such interaction occurs between rubber and radicals derived from azoisobutyronitrile. The very high ratios of grafted to free polymethyl methacrylate obtained in the present work, using aerated natural latex, demonstrate that reactive sites are formed on the rubber hydrocarbon during aeration (or, much more slowly, on storage). It must be concluded also that these reactive sites are formed by the direct action of oxygen on the rubber hydrocarbon. The possibility that oxygen first reacts with some nonrubber constituents of latex forming peroxidic or other reactive intermediates which then attack the rubber (e.g., as benzoyl peroxide has been shown to do) is most unlikely in view of the results in Table II. The reactivity of the aerated latex is clearly associated with the disperse phase of the latex. The rubber particles in the ultracentrifuged cream will still be surrounded by a rather complex adsorbed film of nonrubber constituents which could conceivably react with oxygen, but some at least of these nonrubber constituents would be removed from the surface of the particles when the latex was creamed in the presence of soap. Table II shows that the concentrate obtained by creaming is at least as reactive as the ultracentrifuged concentrate. Furthermore, suitable synthetic latexes which have been aerated are capable of graft polymerization with methyl methacrylate by the same procedure as that described for natural latex.

Support for the view that the reactive sites in the rubber hydrocarbon are hydroperoxide groups has been given in the preceding paper. The present results are fully in accord with this thesis. For example, the efficiency of tetraethylenepentamine and ferrous salts in promoting the graft polymerization of aerated latex with methyl methacrylate is not surprising, since these same reducing agents are well known as activators for organic hydroperoxides in many vinyl polymerizations.

#### ACKNOWLEDGMENTS

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#### SUMMARY

The peroxidic groups produced on the rubber hydrocarbon when oxygen is absorbed by ammonia-preserved latex are capable of initiating the graft polymerization of methyl methacrylate and other vinyl monomers, in the presence of suitable reducing agents. The products so formed contain only small proportions of unbound homopolymer. In the latex state, the products have a much higher wet gel strength and better film forming properties than materials of the same total vinyl polymer content prepared by other methods.

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# THE NATURE OF THE PARTICLE SURFACE IN HEVEA LATEX AND PASTES OF RUBBER HYDROCHLORIDE AND POLYVINYL CHLORIDE \*

G. SCHUUR

RUBBER-STICHTING, DELFT, HOLLAND

## INTRODUCTION

The colloid-chemical properties of natural rubber latex are influenced by many factors, such as the pH, the concentration of surface-active agents and the presence of ions of different kinds. Many of these factors have been studied intensively.

However, it has usually been assumed that the surface of the rubber particles consists of plain hydrocarbon. Up to now it has been impossible to investigate the properties of the surface free from adsorbed soaps and proteins, for the removal of these surface-active agents results in coagulation of the latex. But the latex particles can be obtained in a hard and nontacky form by hydrochlorination and crystallization according to the methods of van Veesen<sup>1</sup> and the author<sup>2</sup>. The various surface-active agents can then be removed by filtering, washing, and extraction with organic solvents, without the loss of the surface by coagulation of the particles.

The reactions of most organic chemical groups with hydrochloric acid are fairly well known and, though the original properties of the surface may be modified to some extent by the hydrochlorination, an investigation of the surface of rubber hydrochloride may give useful information regarding the properties of the original surface of the rubber particles.

A suitable method for studying the nature of the surfaces of various rubber hydrochlorides would be to investigate the rheological properties of concentrated dispersions in organic media. Dispersions in plasticizers were selected, in the first place, because the experimental work is then not complicated by the volatility of the solvents, and secondly, because these dispersions in plasticizers are of some technical interest, since they can be used for the preparation of monofilaments from rubber hydrochloride<sup>3</sup>.

The use of dispersions of polymers in organic media for investigating the colloid-chemical properties of dispersions in oils has the advantage that the surface of these particles can be modified by organic chemical methods. This was often done during the investigation, both with rubber hydrochloride and polyvinyl chloride. The surface was cleaned by washing and extraction with various solvents. It was modified by oxidation, methylation, and reactions with several amines, especially triethanol amine, as will be shown in the following sections.

The investigation of the rheological properties of these resins dispersed in plasticizers has shown that the surface of latex particles is not plain hydrocar-

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bon, but that its properties and chemical composition depend on the type of the latex and on the way in which the latex has been treated and stored prior to hydrochlorination.

### EXPERIMENTAL METHODS

*Preparation of rubber hydrochloride.*—Ammoniated latex with a dry rubber content of about 60% is stabilized with 1.05 g Emulphor 0 per 100 g latex. Emulphor 0 is a nonionic emulsifier, a condensation product of ethylene oxide and oleyl alcohol. The latex is mixed with half its volume of concentrated (36%) hydrochloric acid. Hydrogen chloride is then passed through for about 40 hours until the maximum chlorine content is reached (approx. 32–33% Cl). The temperature is kept at or below 20° C during all these manipulations. All experiments described in this paper have been done with products having this maximum chlorine content.

The hydrochlorination can be followed closely by means of a rapid determination of the density of the particles<sup>4</sup>.

The rubber hydrochloride is then crystallized by heating the latex at 75° C for 30 minutes. The heating should be done gradually in order to avoid excessive foaming by escaping hydrogen chloride. The latex is then cooled to 60° C and precipitated by pouring it into water at 60° C. For 100 g ammoniated latex, 2 l of water was used. The rubber hydrochloride is filtered, washed with distilled water until free from hydrochloric acid, and dried in air at 50° C.

If all manipulations are carried out properly, the latex particles preserve their individuality and a white powder is obtained with a bulkiness of approximately 2.3 ml/g. However, very bulky products may be obtained under certain conditions. For example, if the crystallization prior to coagulation is omitted, the particles will agglomerate to irregular structures during precipitation and a bulkiness up to approximately 5 ml/g may be observed. These agglomerates cannot be redispersed afterwards and very stiff pastes are obtained which are unsuitable for our investigation (see section on Preparation of the Dispersions).

*Extraction of rubber hydrochloride.*—One hundred grams dry rubber hydrochloride and 200 ml ethanol are milled for 24 hours in a laboratory ball mill. The rubber hydrochloride is filtered and extracted for 8 hours in a Soxhlet apparatus with ethanol. The ethanol is replaced by ether and the extraction is continued for 8 hours. The rubber hydrochloride is then dried at 50° C.

*Oxidation of rubber hydrochloride.*—One hundred grams rubber hydrochloride are dispersed in a solution of 20 g potassium dichromate and 20 g concentrated sulfuric acid in 200 ml water in a laboratory ball mill for 8 hours at room temperature. Sometimes a shorter reaction time was used. The polymer is then filtered, washed with distilled water until free from acid, and dried at 50° C in air.

*Methylation of rubber hydrochloride and polyvinyl chloride.*—Methylation of the carboxyl group (according to the formula: R COOH + CH<sub>3</sub>N<sub>2</sub> → R COOCH<sub>3</sub> + N<sub>2</sub>) is done by adding a solution of 4 g diazomethane in 25 g ether to 100 g extracted rubber hydrochloride dispersed in 200 g ether. The mixture is kept at 10° C for 2 hours. The polymer is then filtered, washed with ether, and dried at 50° C in air. The methylation of polyvinyl chloride (P.V.C.) is done in the same manner.

*Addition of extracted impurities or fatty acids to methylated rubber hydrochloride.*—The extracts of 100 g rubber hydrochloride in alcohol and ether, ob-

tained as described above, are evaporated and the residue is dissolved in 200 g ether. This solution is added to 100 g extracted and methylated rubber hydrochloride and mixed in a laboratory ball mill for 4 hours.

The ether is then evaporated. The same experiment was done with a solution of 1.25 g oleic acid and 1.25 g stearic acid in 200 g ether. The methylated rubber hydrochloride particles are thus coated with the extracted impurities or with fatty acids.

*Oxidation of polyvinyl chloride.*—A dispersion is made of 100 g polyvinyl chloride (Solvic 334, I.C.I.) in a solution of 0.5 g Emulphor 0 in 100 g water. A solution of 100 g KOH in 100 ml water is added. The mixture is kept at room temperature for 2 hours. The polyvinyl chloride becomes brown in color because series of conjugated double bonds are formed. The polymer is then filtered, washed, and oxidized in the same way as rubber hydrochloride, the brown color disappearing. The oxidized polyvinyl chloride is washed with ethanol and dried at 50° C.

*Preparation of cyclized rubber.*—One hundred grams latex with a dry rubber content of 60% is stabilized with 1.05 g Emulphor 0. One hundred fifty g gaseous hydrogen fluoride are added at 5° C. The mixture is kept in a polyethylene bottle for 1.5 hours. It is then poured into 1 l of water at room temperature. The hydrogen fluoride is neutralized with a solution of sodium hydroxide. The temperature is kept below 25° C in order to decrease the tendency of the particles to fuse into irregular agglomerates. The cyclized rubber is filtered, washed with distilled water, and washed with ethanol. It is dried at 50° C in vacuo.

*The measurements of the rheological properties of pastes.*—All measurements were carried out by means of a Couette-type viscometer, the "Drage Struktur Viskosimeter", manufactured by the "Chemisches Institut Dr. A. G. Eppele", Zurich.

The apparatus allows the bobs to be rotated at three different speeds, and the apparent viscosities of the pastes were therefore usually measured at three different rates of shear. The measurements were done immediately after the preparation of the pastes because the apparent viscosities increase slightly with time. All measurements were done at 25° C ± 0.2° C.

*The preparation of the dispersions of the resins in plasticizers.*—The preparation of the pastes is the most critical part of the experiments as far as reproducibility is concerned. The pastes were made by two different methods, which will be referred to as methods I and II.

Method I consists of a premixing of the resin and the plasticizer by means of a spatula. The mixture is then passed through a small laboratory Pascal triple roll-mill. The rolls were fixed at a constant distance (0.185 mm). The apparent viscosities of the pastes depend on the number of passes through the mill. Three passes give the best reproducible results and minimum viscosities.

Method II consists of a premixing of the resin with 60 per cent of the plasticizer with a spatula. The paste is then passed three times through the mill. The rest of the plasticizer is then added and the paste is given a single pass through the mill. The investigations were started with pastes made according to method I, but afterwards method II appeared to give more reproducible results and lower viscosities. The amines are mixed with the pastes by means of a spatula. The reaction is fast and no further changes are observed after about 1 minute.

*The reproducibility of the various products and the preparation of pastes.*—To investigate the reproducibility three batches of rubber hydrochloride were

made. Part of each of these batches was extracted. The pastes made from the batches of unextracted rubber hydrochloride showed a good reproducibility, but after extraction the differences between the rheological properties of the pastes were appreciably increased, presumably owing to the fact that a small proportion of the particles fused into irregular agglomerates during extraction and drying. Nevertheless, the reproducibility was sufficiently good for our purposes, as no conclusions were drawn from the absolute values of the apparent viscosities of the pastes, but only from the changes which occurred when the surface was modified, especially with triethanol amine (T.E.A.).

The plasticizers and the other products used were of a good commercial grade, but no measures were taken to purify them further because the apparent viscosities of the pastes are not influenced appreciably by small quantities of soaps, fatty acids, water, or Emulphor O, presumably because the surface of the particles has no tendency to adsorb these substances. The apparent viscosities depend strongly on the amount and type of plasticizer. Pastes of tricresyl phosphate (T.C.P.) and dibutyl phthalate (D.B.P.) have been investigated usually. However, other plasticizers, such as dibutyl sebacate (D.B.S.), Aroclor (chlorinated diphenyl), and paraffin oil behave in a similar manner, i.e., triethanol amine increases the apparent viscosities of all these pastes.

### RESULTS AND DISCUSSION

*Pastes of rubber hydrochloride.*—The apparent viscosity of a paste of rubber hydrochloride can be influenced appreciably by the addition of small quantities of amines. Amines which contain aromatic groups or long aliphatic chains have little influence on the apparent viscosity of a paste prepared from T.C.P.

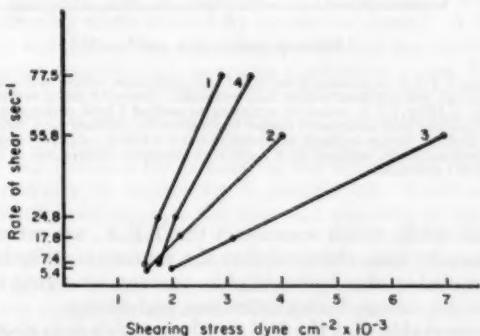


FIG. 1.—Influence of triethanol amine and benzoic acid on a paste of rubber hydrochloride. Curve 1: 100 g rubber hydrochloride in 100 g D.B.P. prepared according to method II. Curve 2: Same as Curve 1 + 0.8 g T.E.A. Curve 3: Same as Curve 1 + 1.2 g T.E.A. Curve 4: Same as Curve 1 + 1.2 g T.E.A. + 2.56 g benzoic acid.

or D.B.P., but these amines may decrease the apparent viscosity of pastes from paraffin oil. On the other hand, amines which contain hydroxyl groups, such as mono-, di-, or triethanol amine, greatly increase the apparent viscosity of the pastes. In particular the stiffening caused by triethanol amine has been used as a criterion in this investigation. It will be referred to as the "T.E.A.-effect" for the sake of brevity.

The stiffening of a paste of 100 g rubber hydrochloride in 100 g D.B.P., prepared according to method II, is shown in Figure 1. The stiffening increases with increasing amounts of T.E.A. until at 1.2 g per 100 g rubber hydrochloride the maximum is reached. Further additions of T.E.A. decrease the apparent viscosity very gradually because the volume of the continuous phase is increased. The stiffening of T.E.A. can be counteracted by the addition of acids. The decrease caused by 2.56 g benzoic acid in a paste, which contained 1.2 g T.E.A., is also shown in Figure 1. Larger amounts of benzoic acid decrease the apparent viscosity still further.

The T.E.A. effect is not caused by impurities which can be removed from the rubber hydrochloride by extraction. A paste of 100 g extracted rubber hydrochloride and 140 g T.C.P., prepared according to method I, shows the maximum stiffening when only 0.2 g T.E.A. is added. Pastes of normal rubber hydrochloride show the maximum stiffening usually after addition of 1 to 1.5 g T.E.A. per 100 g rubber hydrochloride. This difference is presumably due to the fact that fatty acids are always present in normal rubber hydro-

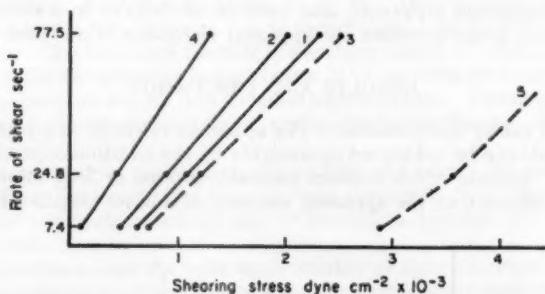


FIG. 2.—Influence of T.E.A. on a paste of extracted and methylated rubber hydrochloride and on pastes of extracted, methylated, and oxidized rubber hydrochloride. Curve 1: 100 g extracted and methylated rubber hydrochloride in 140 g T.C.P., prepared according to method I both without and with 0.5 g T.E.A. Curve 2: 100 g of extracted and methylated rubber hydrochloride, oxidized for 1 hour with potassium dichromate, in 140 g T.C.P. Curve 3: Same as Curve 2 + 0.2 g T.E.A. Curve 4: 100 g of extracted and methylated rubber hydrochloride, oxidized for 8 hours with potassium dichromate, in 140 g T.C.P. Curve 5: Same as Curve 4 + 1 g T.E.A.

chloride. These acids, which counteract the T.E.A., are removed by extraction. It has usually been observed that the maximum stiffening is somewhat smaller for extracted rubber hydrochloride, presumably owing to the fact that some agglomeration occurs during extraction and drying.

It is very remarkable that the T.E.A. effect, which is so clearly observed in pastes of normal and extracted rubber hydrochloride, has completely vanished when pastes of methylated rubber hydrochloride are investigated. This is shown in Figure 2, where Curve 1, obtained from a paste of 100 g methylated rubber hydrochloride in 140 g T.C.P., prepared according to method I, remains unchanged when 0.5 g T.E.A. is added. Large amounts of T.E.A. decrease the apparent viscosity because the volume of the continuous phase is increased.

The T.E.A. effect does not reappear when fatty acids or the extract of normal rubber hydrochloride are added to methylated rubber hydrochloride as described in the experimental section. This is additional evidence that the T.E.A. effect is not caused by extractable impurities.

However, the T.E.A. effect reappears when methylated rubber hydrochloride is oxidized with a potassium dichromate. Curves 2 and 3 in Figure 2 show the stiffening of a paste of methylated rubber hydrochloride, which has been oxidized for 1 hour with a potassium dichromate solution as described in the experimental section. Curves 4 and 5 show the even greater T.E.A. effect after an oxidation for 8 hours. The rubber hydrochloride, which has been oxidized for 1 hour, needed only 0.2 g T.E.A. for maximum stiffening; the rubber hydrochloride, which had been oxidized for 8 hours, needed 1 g T.E.A. Also the T.E.A. effect of normal rubber hydrochloride can be increased by oxidation with potassium dichromate, but, if the oxidized rubber hydrochlorides are methylated, the T.E.A. effect disappears again completely.

Rubber hydrochloride is not oxidized by oxygen in the dark and at room temperature. A methylated rubber hydrochloride did not show a T.E.A. effect after storage for 7 months under these conditions.

*Tentative explanation of the experiments with rubber hydrochloride.*—The experiments carried out with pastes of rubber hydrochloride can be explained qualitatively on the basis of the following assumptions:

- a). Acidic groups, presumably carboxyl groups, are chemically bound to the surface polymer molecules of the rubber hydrochloride particles.
- b). All other things being equal, the minimum apparent viscosity of a dispersion will be observed when the surface of the dispersed phase and the continuous phase are similar.

For instance, a dispersed phase with a polar surface will show a maximum colloid chemical stability and a minimum apparent viscosity in polar liquids, whereas in nonpolar liquids, such as paraffin oil, a maximum apparent viscosity and minimum stability will be observed. (The apparent viscosity is here defined as the shearing stress divided by the rate of shear.) A dispersed phase with a nonpolar surface, on the other hand, will show maximum stability and minimum apparent viscosity in a nonpolar continuous phase, like paraffin oil.

The influence which amines exert on the apparent viscosity of the pastes can readily be explained by the fact that they will react with the carboxyl groups of the surface. Amines with nonpolar aromatic or aliphatic groups (e.g., dibenzylamine) will decrease the polarity of the surface and decrease therefore the apparent viscosity of dispersions in paraffin oil. Triethanol amine will increase the polarity and increase the apparent viscosity of the dispersions in plasticizers.

Methylation of the carboxyl groups makes it impossible for the amines to react with the surface under the prevailing circumstances, and consequently the amines do not change the apparent viscosity of pastes of methylated rubber hydrochloride to any extent.

The T.E.A. effect does not reappear when fatty acids or the extract of rubber hydrochloride is added to methylated rubber hydrochloride, because these substances are not adsorbed by the particles dispersed in plasticizers. But oxidation generates new carboxyl groups on the surface of methylated rubber hydrochloride and the T.E.A. effect therefore reappears.

Organic acids counteract the influence of amines because they compete with the carboxyl groups of the surface and strip the surface of its bound amines if these acids are present in sufficient amounts.

Even rubber hydrochloride, prepared from fresh latex, tapped and stored in the absence of oxygen, shows the T.E.A. effect. On the other hand, the

T.E.A. effect may be increased by an oxidation of the latex by oxygen prior to hydrochlorination, as will be shown afterwards. The carboxyl groups of the surface of rubber hydrochloride may therefore originate from three sources:

a). Part of the carboxyl groups may be the end groups of the natural rubber molecule. This would be in agreement with the formation of natural rubber by a polycondensation of  $\beta$ -methyl-crotonic acid<sup>5,6,7</sup>.

b). Another part of the carboxyl groups may be formed by oxidation of the latex during storage. The carboxyl group will evidently be the last step of the oxidation, and other oxygen-containing groups will probably also be present. These groups will make the surface of the rubber particles more hydrophilic, and they will therefore contribute to the stability of the latex.

c). The carboxyl groups of the surface may also at least partly be explained by the presence of an insoluble acidic compound in the rubber. However, the increase of the T.E.A. effect by oxidation cannot be explained on this basis.

Another conclusion which can be drawn is that not only is the latex stabilized by adsorbed fatty acids and proteins, but chemically bound carboxyl groups may also exert some influence. Moreover, part of the proteins may be chemically bound to the surface by means of the carboxyl groups. This would explain why proteins cannot be completely removed from latex by repeated washing with soap solution.

It is not possible at present to give an exact definition of the similarity which the surface of the dispersed phase and the continuous phase should possess for maximum stability. Nevertheless, the results of this investigation indicate that the properties of these dispersions are not governed only by double-layer repulsion and attraction by long-range London-van der Waals' forces<sup>8</sup>.

Though the particles of rubber hydrochloride are too small to be clearly observed in the electrophoresis apparatus of van der Minne and Hermanie<sup>9</sup>, some preliminary experiments indicated that the particles of oxidized rubber hydrochloride are negative, whereas the particles of methylated rubber hydrochloride appeared to be completely neutral. The negative charge may be due to an ionization of the carboxyl groups. This result is in agreement with Figure 2, the dispersions of oxidized rubber hydrochloride showing the smallest apparent viscosity. In the presence of T.E.A. the dispersions of oxidized rubber hydrochloride show higher apparent viscosities than a paste of methylated rubber hydrochloride. As the particles of methylated rubber hydrochloride are already neutral, this effect cannot be due to a decrease of the double-layer repulsion. It is also impossible to see how small amounts of triethanol amine would increase the long-range London-van der Waals' forces considerably, and it is even more difficult to see how dibenzylamine could decrease these forces in dispersions of rubber hydrochloride in paraffin oil. But these effects can be understood on the assumption that an increase of the polarity of the surface of the particles will increase the colloid chemical stability in polar media and decrease the stability in nonpolar media.

Therefore a more specific attraction, originating from the surface of the particles, seems to be present in these systems, but it is admitted that the experimental evidence is still slight. A systematic investigation of a range of amines and a range of plasticizers with increasing dielectric constant or increasing cohesive energy density could elucidate this point.

*Pastes of polyvinyl chloride.*—If the explanation of the experiments with pastes of rubber hydrochloride is correct, dispersions of other polymers must

show a similar behavior if carboxyl groups are present bound at the surface molecules of the particles.

Therefore a paste-grade polyvinyl chloride (Solvic 334) has been oxidized. Direct oxidation of polyvinyl chloride is very difficult, and much better results are obtained when some hydrogen chloride is removed by means of a concentrated KOH solution prior to oxidation as described in the experimental part.

A paste of normal polyvinyl chloride is not influenced by amines but after oxidation; it behaves indeed in the same way as pastes of rubber hydrochloride. Pastes of oxidized P.V.C. in T.C.P. show no yield value and the increase of the apparent viscosity, when T.E.A. is added, is small. However, a dispersion of 100 g oxidized P.V.C. in 100 g Aroclor 1221 has an initial yield value and a large increase of the apparent viscosity is observed when 0.6 g T.E.A. is added.

Benzoic acid also counteracts the stiffening in pastes of P.V.C., and no T.E.A. effect has been observed in pastes of methylated, oxidized P.V.C. The behavior of oxidized P.V.C. and that of rubber hydrochloride are completely

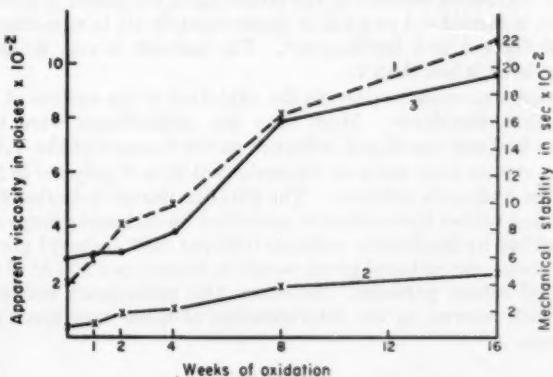


FIG. 3.—The apparent viscosity of pastes of rubber hydrochloride and the mechanical stability of latex as a function of the time of oxidation. Curve 1: Mechanical stability. Curve 2: Apparent viscosity of paste without T.E.A. at a rate of shear of  $7.9 \text{ sec}^{-1}$ . Curve 3: Apparent viscosities after addition of the optimum amounts of T.E.A. at a rate of shear of  $5.7 \text{ sec}^{-1}$ .

similar. To prove that this similarity is caused only by the presence of carboxyl groups at the surface of the particles and is independent of the chemical composition of the interior, a paste of 100 g cyclized rubber in 120 g T.C.P. was investigated. The T.E.A. effect was also observed in this case.

*The oxidation of Hevea latex.*—The oxidation of latex with oxygen was investigated by McGavack and Bevilacqua<sup>10</sup>. They found that the rate of oxidation depends on the pH of the latex. The maximum rate is observed at pH = 10.4. The oxidation is accompanied by a considerable increase of the mechanical stability of the latex.

Though the factors which control the mechanical stability are not fully understood, it seemed quite possible that the bound carboxyl groups and other oxygen-containing groups of the surface of the particles might be important. Therefore an ammoniated latex (pH = 10.4) was oxidized for 16 weeks with air at room temperature. Each day the samples were shaken with air in half-filled bottles for 15 seconds. Care was taken to lose no ammonia. The mechanical stability of the latex after 0, 1, 2, 4, 8, and 16 weeks was determined

according to the A.S.T.M. Designation: 1076-54 T. The samples were also hydrochlorinated and pastes were made of 100 g resin and 100 g D.B.P., according to method II. T.E.A. was added to the pastes until the maximum stiffening was obtained (1 to 2 g T.E.A. per 100 g rubber hydrochloride). The mechanical stability of the latex and the apparent viscosities of the pastes as a function of the time of oxidation of the latex are seen in Figure 3. The apparent viscosities are shown only at a rate of shear of  $7.9 \text{ sec}^{-1}$  in the absence of T.E.A. and at  $5.7 \text{ sec}^{-1}$  with T.E.A., but the viscosities at higher rates of shear showed a very similar trend. This experiment was repeated several times with different latexes. Though some quantitative differences were found, the mechanical stabilities and the apparent viscosities always increased simultaneously. This indicates that bound carboxyl groups and perhaps also other oxygen-containing groups of the surface increase the mechanical stability of the latex.

The influence of the pH of the latex on the rate of oxidation was also investigated. The maximum increase of the stiffening of the pastes is observed when the oxidation is carried out at a pH of approximately 10, in agreement with the results of McGavack and Bevilacqua<sup>10</sup>. The increase is very small when the pH of the latex is less than 7.

An attempt was made to prevent the oxidation of the surface of the rubber particles with antioxidants. More than ten antioxidants were tested, but none of these had any significant influence on the increase of the T.E.A. effect.

Titration curves were made of dispersions of 50 g of polymer in 225 ml of a 0.01 N sodium hydroxide solution. The titration curves indicated that P.V.C. and methylated rubber hydrochloride contained no carboxyl groups whereas an extracted rubber hydrochloride contains 0.03 per cent carboxyl groups, which means that about one carboxyl group would be present per  $200 \text{ \AA}^2$  of the surface of the original rubber particles. However, this preliminary result should be considered with reserve, as the determination of these very small amounts is liable to errors.

#### SYNOPSIS

The apparent viscosity of dispersions of rubber hydrochloride in plasticizers is considerably influenced by amines and by oxidation or methylation of the surface of the particles. Pastes of polyvinyl chloride behave similarly.

The experimental results can be explained by assuming that carboxyl groups are bound to surface polymer molecules of the rubber hydrochloride particles. The number of these carboxyl groups is increased by an oxidation of the original latex with oxygen. The mechanical stability of the latex increases simultaneously.

Indications have been found that the attraction between the particles is at least partly of a more specific character than long-range London-van der Waals' forces.

#### ACKNOWLEDGMENTS

The author is indebted to W. Albers, Utrecht, for his kind assistance with the electrophoresis experiments. The other experiments have been carried out by P. D. Harkes and A. Klootwijk and Miss C. D. Tempelaars. The author wishes to thank the management of the Rubber-Stichting for the permission to publish this paper.

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# MONOLAYER STUDIES OF SOME HYDROXYLATED POLYOLEFIN RUBBERS \*

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## INTRODUCTION

The study of high polymer monolayers by the Langmuir balance technique has been almost wholly restricted to those polymers which contain polar groups, e.g., cellulose, proteins, polyacrylates, etc. Nonpolar polymers do not spread and so little attention has been paid to the hydrocarbon rubbers. Wall and Zelikoff<sup>1</sup> have reported that natural rubber, gutta-percha, and butadiene-styrene copolymers do not form stable monolayers on water, but that when these materials are modified chemically by thiocyanogen they form relatively thin films of varying thickness.

Sivaramakrishnan and Rao<sup>2</sup> have recently confirmed that natural rubber does not form a monolayer on water. However, they find that it spreads spontaneously on a subsolution of aqueous acidic potassium permanganate. We have investigated the surface reaction between certain polyolefins and aqueous permanganate; the kinetic features of these reactions, discussed elsewhere<sup>3</sup>, suggest that definite chemical end-products are formed on the surface. The purpose of this communication is to characterize the end-products obtained from natural rubber (*cis*-1,4-polyisoprene), gutta-percha (*trans*-1,4-polyisoprene), polybutadiene, and two butadiene-styrene copolymers of differing styrene content, when these react under controlled conditions at the surface of an acidic aqueous permanganate subsolution.

## EXPERIMENTAL

The pressure-area ( $\pi$ -A) characteristics of the polymers were studied using a Langmuir-Adam surface balance, as modified by Alexander<sup>4</sup>. The balance was enclosed in an electrically screened, earthed, protective box fitted with external controls. Surface potentials were measured using a radioactive polonium ionizing electrode in conjunction with a balanced double beam tetrode electrometer valve<sup>5</sup>.

The purified polymers were spread from solution (ca. 0.4 mg/ml) in redistilled benzene, using an Agla micromeer syringe. The KMnO<sub>4</sub> was of analytical reagent grade and subsolution water was distilled and passed through charcoal and cationic-anionic exchange resin columns in series. In the kinetic experiments, observations were made at a constant pressure of  $2.0 \pm 0.1$  dyne/cm. Temperature variations during any experiment were  $< \pm 0.2^\circ$  C.

Natural rubber (Hevea pale crepe) was purified by acetone extraction followed by fractional precipitation from chloroform solution with acetone. Infrared examination of the purified polymer showed no detectable oxygen or nitrogen. Purified gutta-percha was kindly supplied by Mr. P. W. Allen of

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British Rubber Producers' Research Association and contained < 0.2 per cent O and 0.02 per cent N. Polybutadiene and two butadiene-styrene copolymers, the latter containing 7.9 and 23.5 per cent (w/w) styrene, respectively, were acetone extracted (dispersed in chloroform and filtered through glass wool to remove gel), and finally fractionally precipitated from chloroform solution with methanol. Infrared examination of the purified products showed no detectable oxygen or nitrogen. In all experiments described here, the subsolution was 0.01 *N* with respect to sulfuric acid.

The kinetic results, shown in Figure 1, were obtained by the following technique. The glass trough of the surface balance was filled with a subsolution of aqueous permanganate and sulfuric acid of known strength. The surface was

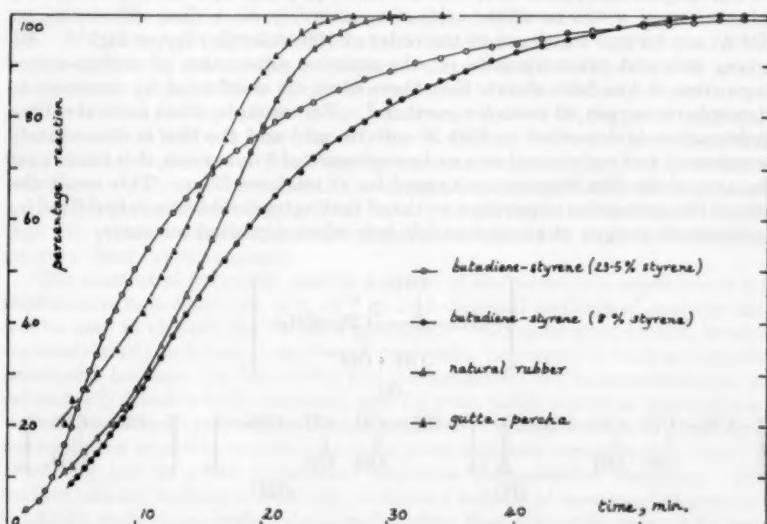


FIG. 1.—Reaction-time curves of polyolefins on acidic permanganate. Subsolution for butadiene-styrene copolymers,  $1.0 \times 10^{-4} N$   $KMnO_4$ ,  $0.01 N$   $H_2SO_4$ . Subsolution for natural rubber and gutta-percha,  $2.0 \times 10^{-4} N$   $KMnO_4$ ,  $0.01 N$   $H_2SO_4$ .

swept several times with paraffin waxed glass slides to adsorb surface impurities, and a calculated amount of polymer solution was deposited with an Agla micrometer syringe. The deposited film was immediately compressed with a waxed slide until the required surface pressure (2 dynes/cm) was registered. This usually took about 1 minute. A stopwatch was started about 15 sec after the first drop of polymer solution had been deposited. The barrier position was continuously adjusted manually from external controls so as to maintain the surface pressure constant at  $2.0 \pm 0.1$  dyne/cm. The extent of reaction was characterized by  $A/A_\infty$ , where  $A$  and  $A_\infty$  are the film areas at times  $t$  and  $\infty$ , respectively. Kinetic results are shown as percentage reaction against time curves. When all reaction (as characterized by the increasing film area) had ceased, the film was momentarily expanded and then slowly compressed to obtain the surface pressure ( $\pi$ ) and surface potential ( $\Delta V$ ) against area isotherms. Surface potential values are not presented here as such. Instead, the

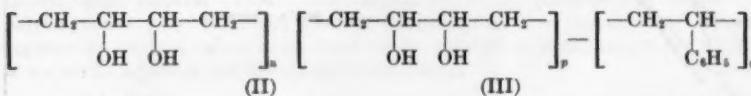
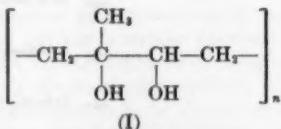
closely related "surface dipole moment ( $\mu$ )" is shown,  $\mu$  values having been calculated by the relationship:

$$\mu = 0.0266\Delta V \cdot A$$

where  $\Delta V$  units are millivolts,  $A$  units are square angstrom units per polymer residue, and  $\mu$  units are millidebyes.  $\mu$  is a measure of the vertical component (i.e., normal to the surface) of the dipole moment per residue of hydroxylated polymer.

### RESULTS AND DISCUSSION

*The surface hydroxylation reaction.*—When polyisoprenes are deposited on a subsolution of water or dilute acid, comparatively thick films (thickness ca. 500 Å) are formed which are of the order of 100 molecular layers high<sup>2,6</sup>. By taking stringent precautions to rid the aqueous subsolution of surface-active impurities, it has been shown that these films are unaffected by exposure to atmospheric oxygen, at room temperature<sup>7</sup>. For example, when natural rubber hydrocarbon is deposited on 0.01 N sulfuric acid and the film is immediately compressed and maintained at a surface pressure of 2 dynes/cm, it is found that the area of the film remains unchanged for at least one hour. This result disproves the contention of previous workers<sup>2</sup> that natural rubber is autoxidized by atmospheric oxygen at an appreciable rate when deposited on water.



When natural rubber hydrocarbon and similar polyolefins are deposited on acidified aqueous potassium permanganate, the polymers spread spontaneously at measurable rates to form monolayers whose final areas are characteristic of the polyolefin. By analogy with the well-established surface hydroxylation of unsaturated amphipathic molecules (e.g., fatty acids and esters<sup>8,9</sup>), it may be suggested with confidence that this spontaneous expansion results from a chemical reaction between the polyolefin and the aqueous acidic permanganate. For natural rubber, the initial product of this reaction corresponds to poly-2-methyl-2,3-dihydroxybutane (I), which being a polyglycol, would be expected to form an orientated unimolecular film at the air/subsolution interface. The analogous glycols for polybutadiene and polybutadiene-styrene copolymers are II and III, respectively, where  $n$ ,  $p$ , and  $q$  are the usual parameters describing polymer composition.

In common with the analogous reaction of permanganate with olefinic fatty acids and esters, the expansion reaction of the polyolefins is followed by a slower reaction, involving oxidative scission of the polymer main chain, during which the monolayer dissolves in the subsolution, and the monolayer area (at constant pressure) decreases steadily. Unless the permanganate concentration is ex-

tremely low, it is impossible to isolate kinetically the primary hydroxylation reaction. Exploratory experiments showed that a permanganate concentration of about  $10^{-4} N$  was well suited to allow the reaction to proceed at a convenient rate while preventing subsequent oxidative scission reactions. Figure 1 illustrates reaction-time curves for natural rubber, gutta-percha, and two butadiene-styrene copolymers (styrene content = 8 and 23.5 per cent, i.e.,  $p/q = 22.2$  and 6.3, respectively). Subsolutions were:  $2.0 \times 10^{-4} N$   $KMnO_4$  for the polyisoprenes,  $1.0 \times 10^{-4} N$   $KMnO_4$  for the copolymers and, in all cases,  $0.01 N H_2SO_4$ . It can be seen that the reaction proceeds to completion in every case, thereby demonstrating the effectiveness of subsolution conditions in isolating the primary reaction.

The kinetic form of the reaction-time curves is of interest and a kinetic analysis for the polyisoprenes has been described elsewhere<sup>3</sup>. It is noteworthy that the kinetic form of the reaction of the butadiene-styrene copolymers differs appreciably from that of the polyisoprenes, in that the maximum rate occurs much sooner (e.g., at 20 → 30 per cent reaction) for the butadiene-styrene copolymers than for the polyisoprenes (maximum rate at 50 per cent reaction). The same effect has been found for polybutadiene, and this we believe arises from the differing double-bond reactivity toward permanganate of the 1,2- and 1,4-butadiene residues. The detailed kinetics of the polybutadiene-permanganate reaction will be described at a later date. At present, it is sufficient to note that the primary reaction has been isolated and is found to go to completion on very dilute permanganate.

The amount of polyolefin used in any one of the monolayer experiments described here is so small (ca.  $5 \times 10^{-6} g$ ) that chemical methods of analysis cannot be used to identify the reaction products. Analogous experiments, involving analytically sufficient quantities of polyolefin, performed in bulk are equally unsatisfactory because: (a) polyolefins and permanganate are incompatible and no solvent will dissolve both reactants, and (b) even if this objection were circumvented by using an emulsion system, a prohibitively large volume of permanganate solution would be required since the permanganate concentration must be extremely low to avoid subsequent oxidative chain-scission reactions. The surface balance technique, however, provides a method of investigating reaction products, such as the hydroxylated polyolefins, that cannot be isolated by conventional methods of "bulk" chemistry. From a study of the surface pressure area ( $\pi\text{-}A$ ) and surface moment-area ( $\mu\text{-}A$ ) characteristics of the products, it is possible to derive information concerning their structure and orientation at the surface. For example, it is known that high polymers containing hydrophilic polar groups ( $-\text{OH}$ ,  $\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{R}$ ,  $\text{CN}$ , etc.) form stable monomolecular layers at an air-water interface<sup>10</sup>. Such monolayers are oriented for maximum surface stability with their polar groups directed toward, and their nonpolar groups directed away from, the aqueous subsolution. On this basis, products such as I, II, and III are expected to form oriented monolayers with their main chains resting along the surface and with their hydroxyl groups directed into the subsolution. The extent to which this occurs in practice can be estimated by comparing the observed area occupied by a hydroxylated polyolefin residue with the area per residue calculated on the basis of established interatomic distances.

*Film characteristics of hydroxylated polyisoprenes (I).*—Natural rubber hydrocarbon was deposited on  $1.0 \times 10^{-4} N$   $KMnO_4$  subsolution, the expansion reaction was allowed to proceed until the area became constant (ca. 80 min), the resultant film was compressed, and the  $\pi\text{-}A$  and  $\mu\text{-}A$  characteristics were determined. These are shown in Figure 2, where it can be seen that the film is

highly condensed. Gentle exploration of the film with a fine air jet showed that the film was completely mobile over the whole of the compression region. The limiting area of the film (i.e., the area per residue obtained by extrapolating the linear, high pressure region down to zero pressure) is  $24.0 \text{ \AA}^2$  per residue.

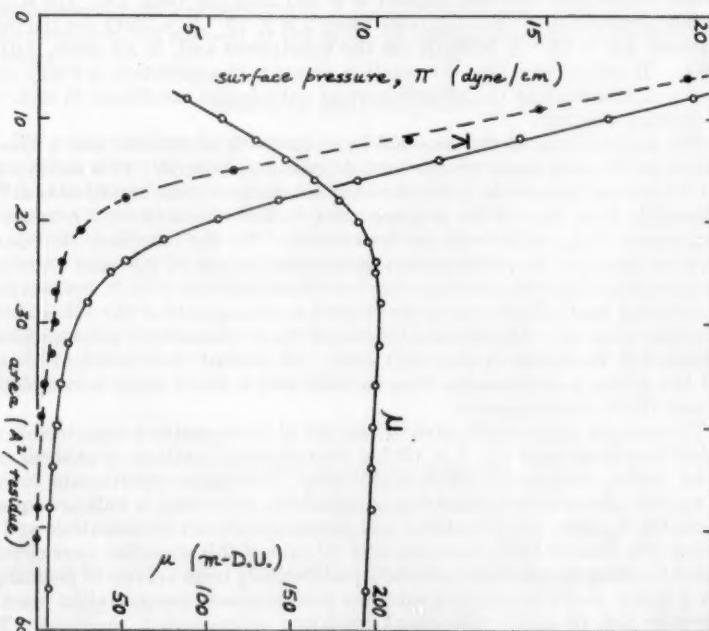
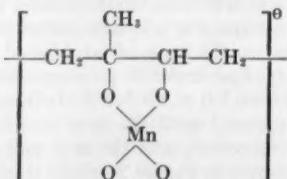


FIG. 2.—Surface pressure ( $\pi$ - $A$ ) and surface dipole moment ( $\mu$ - $A$ ) curves for natural rubber (○) and gutta percha (●). Subsolution for natural rubber,  $1.0 \times 10^{-4} N$  KMnO<sub>4</sub>,  $0.01 N$  H<sub>2</sub>SO<sub>4</sub>. Subsolution for gutta percha,  $2.0 \times 10^{-4} N$  KMnO<sub>4</sub>,  $0.01 N$  H<sub>2</sub>SO<sub>4</sub>.

$\mu$  can be seen to remain virtually constant, at about 200 millidebyes, at areas greater than  $25 \text{ \AA}^2$  per residue, thus demonstrating the homogeneity of the expanded film and the absence of hydroxyl group reorientation on compression over this region. The large drop in  $\mu$  occurring on compression below  $25 \text{ \AA}^2$  shows that considerable distortion, involving a reorientation of the originally fully extended residues, occurs in the high pressure region. To exclude the possibility of the primary reaction product being a polyisoprene permanganate addition complex, e.g.:



a further experiment was performed in which the surface reaction was taken to completion and sufficient sodium sulfite was then added to the subsolution to reduce completely the permanganate (disappearance of purple color). Such a process should also destroy any addition complex that might be present. The resultant film was then compressed and its surface characteristics determined. It was found that the destruction of the permanganate by the sulfite produced no detectable effect on either the  $\pi$ -A or the  $\mu$ -A characteristics of the film. It is concluded that the primary reaction product is not an olefin/permanganate addition complex.

When natural rubber hydrocarbon is deposited on more concentrated permanganate subsolutions, the expansion reaction proceeds at a greater rate. For example, on 0.01 N KMnO<sub>4</sub>, the reaction is complete within two minutes and, if the resultant film is immediately compressed, its surface characteristics can be determined before appreciable chain scission has occurred. Figure 3

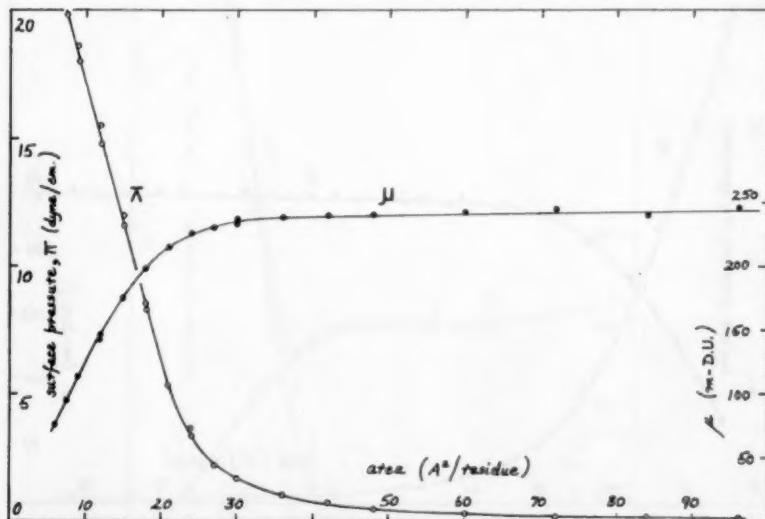


FIG. 3.—Surface pressure (○) and surface dipole moment (●) curves for natural rubber.  
Subsolution: 0.01 N KMnO<sub>4</sub>, 0.01 N H<sub>2</sub>SO<sub>4</sub>.

shows the  $\pi$ -A and  $\mu$ -A curves obtained under these conditions. Each curve contains points from two separate experiments and it is evident that the results are wholly reproducible. Although the film is somewhat more expanded in the low pressure region than that obtained on  $1.0 \times 10^{-4}$  N KMnO<sub>4</sub>, the limiting area is found to be 25.5  $\text{A}^2$  per residue. This value is sufficiently close to that (24.0  $\text{A}^2/\text{res.}$ ) obtained on  $1.0 \times 10^{-4}$  N KMnO<sub>4</sub> subsolution to permit the conclusion that the reaction product is a well-defined entity. The more expanded nature and the high compressibility of the film on the stronger permanganate subsolution suggests that a certain amount of chain scission has occurred during the short time (ca. 10 min) necessary to determine the  $\pi$ -A and  $\mu$ -A curves. This view receives support from the higher value of  $\mu$  (ca. 240 millidebyes) in the expanded region on the stronger permanganate subsolution. This value,

corresponding to a more complete vertical orientation of the hydroxyl groups in the surface, is understandable on the basis of the greater orientational freedom of the polymer end-groups and their neighbors in the same chain.

Gutta percha differs from rubber in that reproducible limiting areas could not be obtained after reaction on very dilute permanganate. Figure 2 shows a typical  $\pi$ - $A$  curve, on  $2.0 \times 10^{-4} N$  KMnO<sub>4</sub>, having an apparent limiting area of  $19 \text{ A}^2$  per residue. Values ranging from 7 through to  $23 \text{ A}^2$  per residue were found in repeat experiments. Further study showed that the larger areas were obtained when the gutta solution was warmed immediately prior to deposition or when the gutta was "plasticized" with liquid paraffin. This incomplete spreading undoubtedly results from the strong tendency of gutta to crystallize in both the spreading solution and the initially deposited films. The high cohesion of the crystallites reduces the ability of the hydroxylated resi-

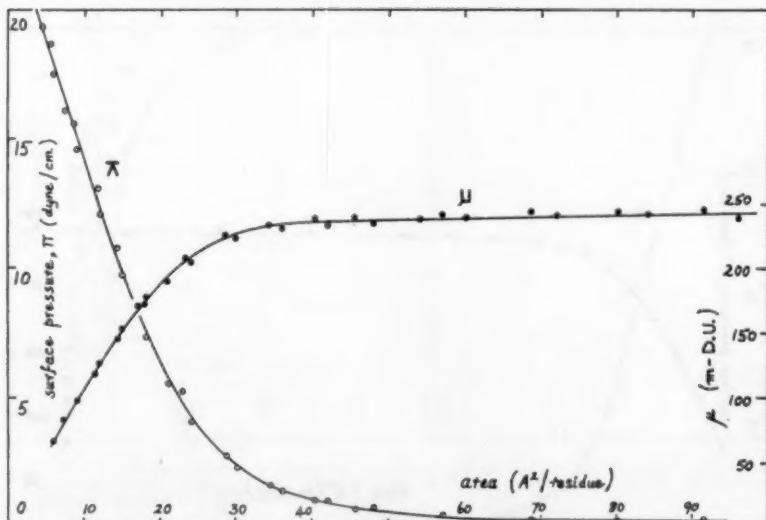


FIG. 4.—Surface pressure (○) and surface dipole moment (●) curves for gutta-percha.  
Subsolution: 0.01 N KMnO<sub>4</sub>, 0.01 N Na<sub>2</sub>SO<sub>4</sub>.

dues to spread out on the surface and bring further unreacted residues into kinetic contact with the permanganate in the subsolution. This difficulty was successfully overcome by depositing the gutta on 0.01 N KMnO<sub>4</sub>. Under these conditions, the rate of hydroxylation is so great that, by the time the volatile solvent has evaporated, the residual film is extensively hydroxylated and is therefore a random copolymer of isoprene and dihydroxyisoprene. Such a copolymer, with its nonregular chain structure could not crystallize on the surface, and the hydroxylation should therefore proceed to completion. Figure 4 shows the  $\pi$ - $A$  and  $\mu$ - $A$  characteristics of gutta, deposited on 0.01 N KMnO<sub>4</sub>. Aside from minor differences in compressibility and higher pressure stability, the resultant film is remarkably similar to that obtained from rubber in its limiting area ( $25.8 \text{ A}^2$  per residue) and  $\mu$  (240 millidebyes) in the expanded region. Referring back to Figure 2, and assuming that hydroxylated gutta

possesses the same limiting area as hydroxylated rubber, a corrected value of  $\mu$  can be calculated for hydroxylated gutta, on  $2.0 \times 10^{-4} N$  KMnO<sub>4</sub>. This corrected value, 201 millidebyes, is virtually identical with that found for hydroxylated rubber, 200 millidebyes.

*Film characteristics of hydroxylated polybutadiene (II) and butadiene-styrene copolymers (III).*—Following the above technique,  $\pi$ -A and  $\mu$ -A curves were constructed for the hydroxylation products of polybutadiene and the butadiene-styrene copolymers. These are presented in Figure 5 (subsolution:  $1.0 \times 10^{-4}$

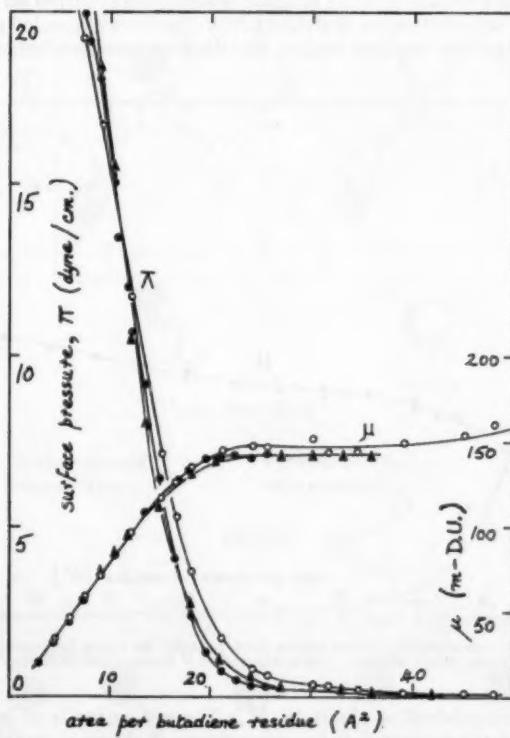


Fig. 5.—Surface pressure ( $\pi$ -A) and surface dipole moment ( $\mu$ -A) curves for polybutadiene ( $\blacktriangle$ ), polybutadiene-styrene (5% styrene,  $\circ$ ), and polybutadiene-styrene (23.5% styrene,  $\bullet$ ). Subsolution:  $1.0 \times 10^{-4} N$  KMnO<sub>4</sub>,  $0.01 N$  H<sub>2</sub>SO<sub>4</sub>.

$N$  KMnO<sub>4</sub>) and Figure 6 (subsolution:  $0.01 N$  KMnO<sub>4</sub>), where the film areas are expressed in terms of the area occupied per butadiene residue. Figure 5 shows that, on very dilute permanganate, there is no significant difference between polybutadiene and the copolymers, i.e., the presence of styrene residues in the polymer has no effect on the surface characteristics of the reaction products; this must mean that the styrene residues are not present in the effective surface phase. On average, for these three polymers, the limiting area per butadiene residue is  $18.5 \pm 1.0 \text{ } \text{\AA}^2$ . Since the  $\mu$  values (ca. 145 millidebyes) of the buta-

diene polymers differ appreciably from the polyisoprenes (ca. 200 millidebyes), and are independent of the styrene content, this difference must be ascribed to a difference in hydroxyl group orientation between the butadiene polymers and the polyisoprenes. This is not surprising in view of the fact that about 20 per cent of the butadiene residues are 1,2 polymerized.

Figure 6 shows  $\pi$ - $A$  and  $\mu$ - $A$  curves for a butadiene-styrene copolymer, containing 23.5 per cent styrene, after hydroxylation on  $0.01\text{ N KMnO}_4$ . On this subsolution the copolymer has a limiting area of  $19.0\text{ A}^2$  per butadiene residue, a value which is very close to that ( $18.5\text{ A}^2$ ) formed on  $1.0 \times 10^{-4}\text{ N KMnO}_4$ . Thus, although a certain amount of chain scission has occurred on the stronger permanganate subsolution, as is evident from the more expanded nature of the  $\pi$ - $A$  curve in the low pressure region, the limiting area per butadiene residue

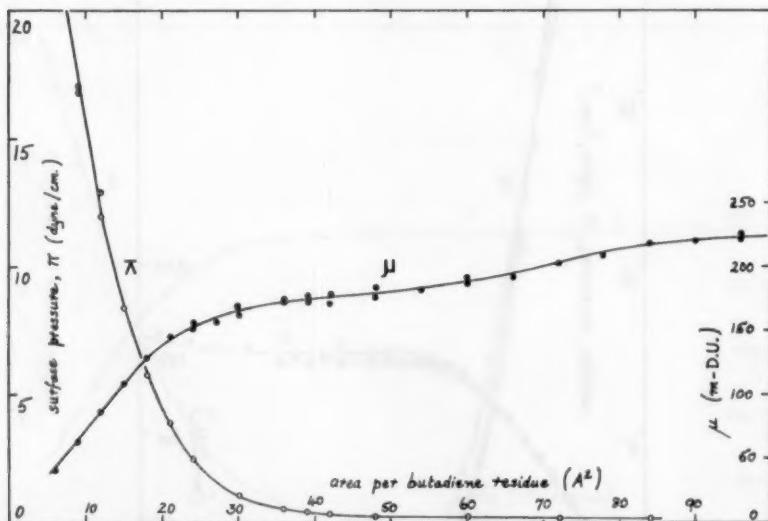


FIG. 6.—Surface pressure (○) and surface dipole moment (●) curves for polybutadiene-styrene (23.5% styrene). Subsolution:  $0.01\text{ N KMnO}_4$ ,  $0.01\text{ N H}_2\text{SO}_4$ .

remains well established at about  $19\text{ A}^2$ . The  $\mu$ - $A$  curve is of interest since, unlike those of the hydroxylated polyisoprenes, it shows a marked reduction from 225 down to 174 millidebyes, as the film is compressed from 100 down to  $40\text{ A}^2$ . This may be a reflection of the reorientation of the pendant 1,2 residues on compression, although the possibility of the styrene residues contributing to the surface dipole moment, in the expanded region, cannot be excluded. As with the polyisoprenes,  $\mu$  values on  $0.01\text{ N KMnO}_4$  are significantly higher than those on  $1.0 \times 10^{-4}\text{ N KMnO}_4$ , and this may be due to more complete hydroxyl group orientation resulting from chain scission.

*Structure of hydroxylated polyolefin films.*—In view of the incursion of chain-scission reactions when hydroxylation proceeds on the stronger permanganate subsolutions, the following comments are largely limited to the results obtained on the more dilute subsolutions.

The first fact that emerges is that the hydroxylated films are monomolecular layers. This can be shown directly from considerations based on accepted covalent bond radii<sup>12</sup> or from molecular models constructed to these dimensions. Using the following covalent bond parameters: C—C 1.54 Å, C—H 1.07 Å, C—O 1.42 Å, O—H 0.96 Å, >C 110°, an idealized diagram of a hydroxylated 1:4 butadiene residue can be constructed (see Figure 7). This diagram is idealized in the sense that a regular arrangement has been postulated in which

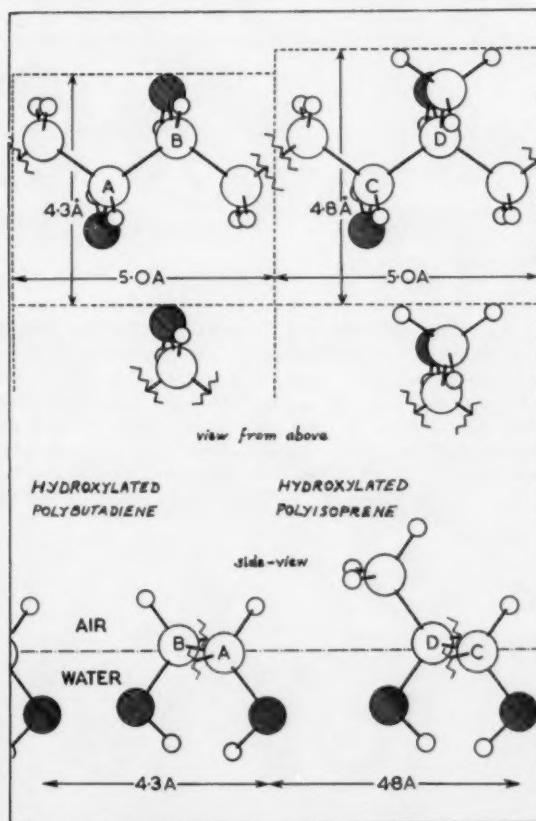


Fig. 7.—Orientation of hydroxylated polybutadiene and polyisoprene at the aqueous subsolution/air interface. Small circles: hydrogen. Large circles: carbon. Shaded circles: oxygen.

the carbon valencies are "staggered"<sup>13</sup>. This results in an orientation in which the hydroxyl groups are directed toward the aqueous subsolution, as required by the formation of a stable surface film. Such an arrangement possesses a residual repeat distance of 5.0 Å along the polymer chain and a distance of 4.3 Å normal to the chain direction. The former distance is determined exclusively by C—C covalent bond distances and angles, while the latter distance is deter-

mined largely by the less well-defined van der Waals radii. The calculated surface area of such an idealized residue is  $21.5 \text{ \AA}^2$ . This value may be compared with the residual areas found experimentally, about  $19 \text{ \AA}^2$  (see Table I). The experimental values are somewhat lower than the calculated value, but this discrepancy may easily be accommodated by allowing for the limited

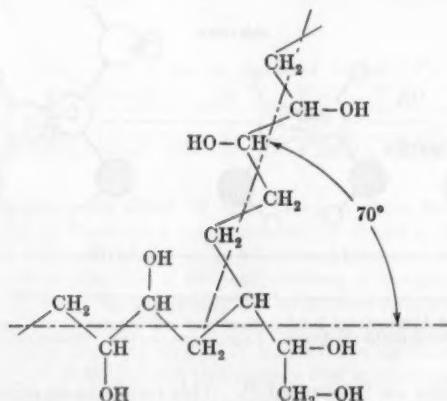
TABLE I  
LIMITING AREAS AND SURFACE DIPOLE MOMENTS OF  
HYDROXYLATED POLYOLEFINS ON ACIDIFIED  
( $0.01 \text{ N H}_2\text{SO}_4$ ) POTASSIUM PERMANGANATE SUBSOLUTIONS

Polyolefin	Limiting area ( $\text{\AA}^2/\text{res.}$ )		(Millidebyes at $35 \text{ \AA}^2/\text{res.}$ )	
	$1.0 \times 10^{-4}$ $N \text{ KMnO}_4$	$0.01$ $N \text{ KMnO}_4$	$1.0 \times 10^{-4}$ $N \text{ KMnO}_4$	$0.01$ $N \text{ KMnO}_4$
Natural rubber	24.0	25.5	200	236
Gutta percha	(24.0) <sup>a</sup>	25.8	(201) <sup>b</sup>	239
Polybutadiene	17.5	—	140	—
Butadiene (92%)-styrene (8%)	19.5	—	148	—
Butadiene (76.5%)-styrene (23.5%)	18.5	19.0	142	174

<sup>a</sup> Assumed value (see earlier discussion).

<sup>b</sup> Calculated value based on assumed value. Subsolution:  $2.0 \times 10^{-4} \text{ N KMnO}_4$ .

amounts of main chain rotation and interchain distortion that undoubtedly occur when the film is compressed laterally. The extent to which the presence of 1,2 units affects the average residual area is unknown, but molecular models suggest that the area occupied by a fully extended 1,2 residue should not appreciably differ from that of a 1,4 residue. However, the presence of a 1,2 residue in the long chain introduces orientational problems that can be overcome only by the existence of kinks of the following type, in which a  $70^\circ$  change of direction, in the surface plane, is involved. Since each of the hydroxylated



carbon atoms is stereochemically asymmetric, each residue may contain an *erythro* or a *threo* pair of —OH groups. Not enough is known about the mechanism of hydroxylation by acidic permanganate to decide this matter. How-

ever, structures based on atomic models suggest that no significant difference in the calculated residual areas of these two forms is to be expected. On the whole, in view of these problems of isomerism, the difference between the calculated and experimental residual areas is gratifyingly small, and it may be safely concluded that the resultant film is a monomolecular layer.

As already mentioned, the styrene content of the copolymers, is without effect on both the limiting area and the surface dipole moment. Since a phenyl group would occupy at least  $25 \text{ A}^2$  in the surface, it is evident that the styrene residues must be situated either above or below the hydroxylated butadiene residues. This result is surprising since one would expect an isolated styrene residue, flanked by hydroxylated butadiene residues, to be extended in the surface, and it must be concluded that a high proportion of the styrene is in the form of groups of contiguous styrene residues. The work of cohesion of a block of styrene residues would exceed its work of adhesion to water and such a block would therefore not occupy an appreciable area on the surface (cf. polyolefins before hydroxylation). This concept would account for the results of Rabjohn<sup>14</sup> et al., who, by the ozonolysis of GR-S, were able to identify only one in four styrenes as isolated residues along the copolymer chain.

The polyisoprenes, considered here, contain only one chemical type (1,4) of repeat unit and the surface dimensions of their hydroxylated derivatives are, therefore, correspondingly simpler to predict. The repeat distance along the chain is  $5.0 \text{ \AA}$ , as for the hydroxylated polybutadienes, but the interchain distance is expected to be greater than that of the hydroxylated polybutadienes owing to the presence of the methyl group. Referring back to Figure 7 it can be seen that the interchain distance of the polybutadiene derivatives is determined by the nearest approach of the hydroxyl groups in neighboring chains. A hydroxylated isoprene residue, however, of identical "idealized" orientation is unable to approach its neighboring chain so closely (see Figure 7). The replacement of a hydrogen by a methyl group in the residue increases the interchain distance (van der Waals radius of  $\text{H} = 1.2 \text{ \AA}$ ,  $\text{CH}_3 = 2.0 \text{ \AA}$ ) which is now determined by the nearest approach of a methyl group to a neighboring methylene group. The resultant interchain distance,  $4.8 \text{ \AA}$ , gives an area of  $24.0 \text{ A}^2$  per hydroxylated isoprene residue. This calculated value is in excellent agreement with the experimental values (see Table I) of  $24 \text{ A}^2$  and ca.  $25.5 \text{ A}^2$  found on  $1.0 \times 10^{-4} N$  and  $0.01 N \text{ KMnO}_4$ , respectively. The concept is idealized insofar as packing differences due to *threo* and *erythro* forms are neglected. It is of interest, however, that both *cis*- and *trans*-polyisoprenes appear to yield the same hydroxylated derivative—insofar as these may be characterized by their limiting areas and surface dipole moments.

The surface dipole moments of the polybutadienes are consistently lower, by about 60 millidebyes, than those of the polyisoprenes. This is probably a result of the orientational distortion associated with the presence of 1,2 units along the chain. As previously mentioned, such groups—while not affecting the limiting areas—introduce kinks into the chain. These kinks will produce a less complete vertical orientation of the hydroxyl groups, and hence a smaller dipole moment normal to the surface. This interpretation is supported by preliminary results obtained with a synthetic polyisoprene containing about 10 per cent of 1,2 and 3,4 units. This polymer, when hydroxylated, possesses a limiting area identical with the hydroxylated natural polyisoprenes, but with a markedly reduced surface dipole moment.

## SYNOPSIS

When thin films of natural rubber, gutta percha, polybutadiene, and polybutadiene-styrene copolymers are deposited at the surface of aqueous acidified potassium permanganate, they undergo a surface reaction and spread spontaneously. A study of the products of this reaction has been made, and their surface characteristics are described. The reaction products are polyhydroxy derivatives of the polyolefins and are shown to form stable monomolecular layers at an air-water interface. The areas of the hydroxylated olefin residues have been determined, and their magnitude and orientation at the interface is discussed. The agreement between experimentally determined areas and theoretical areas (from established interatomic distances) is good. Results suggest that butadiene-styrene copolymers contain an appreciable number of blocks of contiguous styrene units.

## ACKNOWLEDGMENTS

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# GLASS TRANSITION TEMPERATURES OF COPOLYMERS \*

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## I. INTRODUCTION

As the temperature is lowered, the expansivity of all polymers, even in the absence of crystallinity, decreases from a value of about that of a normal liquid to a value near that of a normal crystalline solid. The determination of glass transition temperature as the intersection of linear portions of graphs of volume or length against temperature is a familiar procedure, and the value obtained is of course a highly significant parameter for a polymer.

In discussing the glass transition temperature of a copolymer, the first point to be made is that it exists; that is, a true copolymer possesses a single glass transition temperature. With mechanical mixtures not forming true solutions and with graft and block copolymers this is not so, and under favorable conditions one can observe breaks in the volume-temperature relation corresponding to the glass transitions of the separate constituents<sup>1</sup>. The present paper presents an analysis of available experimental data on the dependence of glass transition temperature on composition in copolymers.

## II. FORMS OF GENERAL EQUATION

The simplest relationship one can conceive would set  $\theta$ , the glass transition temperature of the copolymer, equal to the properly-weighted average of  $\theta_1$  and  $\theta_2$ , the glass transition temperatures of the homopolymers made from the respective constituents. For uniformity  $\theta_2$  will be taken as greater than  $\theta_1$ . It would seem reasonable that the weighting factor of a given constituent  $i$  should include  $c_i$ , the weight-fraction of that constituent, and a constant  $A_i$  characteristic of the constituent in some manner as yet unspecified. Thus for a copolymer

$$A_1c_1(\theta - \theta_1) + A_2c_2(\theta - \theta_2) = 0 \quad (1)$$

A system containing three or more components would be represented by an equation with additional terms of the same type.

It will be seen in the next section that equations equivalent to Equation (1) can be derived from several theoretical approaches. The derivations differ in the significance to be ascribed to the factors  $A_1$  and  $A_2$ . The form of Equation (1) shown here, in view of its symmetry and simplicity, is regarded as the most satisfactory general presentation. For special purposes, however, the equation can be put into many different forms. The equivalence of these forms has not always been recognized.

If one defines a constant  $k = A_2/A_1$ , a form which is explicit for  $\theta$  is:

$$\theta = [\theta_1 + (k\theta_2 - \theta_1)c_2]/[1 - (1 - k)c_2] \quad (2)$$

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It can readily be noted from this form that if and only if  $A_2 = A_1$  will  $k$  be unity and the relation between  $\theta$  and  $c_2$  be linear. Gordon and Taylor<sup>2</sup>, who were apparently the first to publish a relation between  $\theta$  and  $c_2$ , presented the relation in a form like Equation (2), differing only in that it was explicit for  $c_2$ .

The slope of a plot of  $\theta$  against  $c_2$  has the limiting values of  $k(\theta_2 - \theta_1)$  at  $c_2 = 0$  and  $(1/k)(\theta_2 - \theta_1)$  at  $c_2 = 1$ . It will be noted later that  $k$  is almost always less than unity. Consequently the initial slope will usually be less than the average slope and the final slope greater than the average. Thus the plot will usually be convex to the axis of abscissas.

If one defines a constant  $R = (\theta_2 A_2)/(\theta_1 A_1) = (\theta_2/\theta_1)k$ , Equation (1) can be put in a reciprocal form given by Mandelkern<sup>3</sup> et al. With the correction of a slight typographical error, the equation is:

$$1/\theta = [1/(c_1 + R c_2)][c_1/\theta_1 + R c_2/\theta_2] \quad (3)$$

For the special case where  $R = 1$ , namely if  $k = \theta_1/\theta_2$ , this readily reduces to the simple equation given by Fox<sup>4</sup>:

$$1/\theta = c_1/\theta_1 + c_2/\theta_2 \quad (4)$$

Equation (1) can be put in a form involving volume-fraction  $v$  rather than weight-fraction  $c$  if desired, by introducing the density  $\rho$  of the homopolymer at the temperature  $\theta$ .

$$A_1 \rho_1 v_1(\theta - \theta_1) + A_2 \rho_2 v_2(\theta - \theta_2) = 0 \quad (5)$$

A plot of  $\theta$  against  $v_2$  will be linear if  $A_2 \rho_2 = A_1 \rho_1$ , or, in other words, if  $k = \rho_1/\rho_2$ . Since this condition is generally not fulfilled, no advantage is found in using Equation (5) instead of Equation (1).

Equation (1) can also be put in a form involving mole-fraction  $n$  rather than weight-fraction  $c$ , if desired, by introducing the molecular weight  $M$  of the repeating unit of each homopolymer:

$$A_1 M_1 n_1(\theta - \theta_1) + A_2 M_2 n_2(\theta - \theta_2) = 0 \quad (6)$$

A plot of  $\theta$  against  $n_2$  will be linear if  $A_1 M_1 = A_2 M_2$  or, in other words, if  $k = M_1/M_2$ . Since this condition is generally not fulfilled no advantage is found in using Equation (6) instead of Equation (1).

### III. DERIVATION OF EQUATION

Gordon and Taylor<sup>2</sup> were the first to discuss the relation. They examined the consequences of assuming that in an ideal copolymer (analogous to an ideal solution) the partial specific volumes of the components are constant and equal to the specific volumes of the two homopolymers. They assume further that the specific volume-temperature coefficients for the two components in the rubbery and glassy states remain the same in the copolymers as in the homopolymers and are not functions of temperature. At the glass transition temperature of the copolymer they then equate the specific volume of the copolymer in the glassy state to the specific volume in the rubbery state. The resulting equation is essentially Equation (2) with  $A_1 = \beta_{1r} - \beta_{1g}$  and  $A_2 = \beta_{2r} - \beta_{2g}$ . This is, in each case, the difference of the specific volume-tempera-

ture coefficients above and below the glass transition of the homopolymer (i.e., in the rubbery and glassy states, respectively).

Mandelkern and coworkers<sup>3</sup>, giving considerable credit to unpublished work of Fox, have reported a different derivation based on considerations of specific volume as the sum of a "free volume" and an "occupied volume", each with its own temperature coefficient. Like Gordon and Taylor, they assume that the partial specific volumes are constant and are equal to those of the homopolymers. Proceeding from the evidence of Fox and Flory<sup>5</sup> that the glass transition occurs at a constant value of "free volume," Williams, Landel, and Ferry<sup>6</sup> conclude that this point is reached when the free volume has been reduced to a certain small fraction  $k_w$  of the total specific volume. They evaluated this fraction as about 0.025. Mandelkern and his colleagues utilized these considerations to derive Equation (3).

The significance of the constants is as follows:

$$A_1 = \beta_{1r} - k_w\beta_{1r} - \beta_1^*$$

and

$$A_2 = \beta_{2r} - k_w\beta_{2r} - \beta_2^*$$

where  $\beta_1^*$  and  $\beta_2^*$  are the volume-temperature coefficients of the occupied volume per unit mass of the respective homopolymers. Of course, if the term involving  $k_w$  is omitted (as being only about 2.5 per cent of the preceding term) and if  $\beta_1^*$  can be taken as the same as  $\beta_{1g}$  with  $\beta_2^*$  the same as  $\beta_{2g}$ , the significance of  $A_1$  and  $A_2$  is the same as that of the constants obtained by the derivation of Gordon and Taylor. Mandelkern and coworkers regarded the available experimental determinations of the quantities entering into  $A_1$  and  $A_2$  as so unsatisfactory that they recommended that  $R$  be considered an arbitrary parameter.

#### IV. EXPERIMENTAL DATA FOR TYPICAL COPOLYMERS

For plotting observations of  $\theta$  as a function of composition in two-component systems, the most convenient forms of Equation (1) appear to be

$$\theta = k(\theta_2 - \theta)(c_2)/(1 - c_2) + \theta_1 \quad (7)$$

and

$$\theta = -(1/k)(\theta - \theta_1)(1 - c_2)/c_2 + \theta_2 \quad (8)$$

Equation (7), suitable for use when  $\theta_2$  is known, calls for linearity in a plot of  $\theta$  against  $(\theta_2 - \theta)(c_2)/(1 - c_2)$ . The slope of such a plot is  $k$  and the intercept is  $\theta_1$ . Similarly Equation (8), suitable for use when  $\theta_1$  is known, calls for linearity in a plot of  $\theta$  against  $(\theta - \theta_1)(1 - c_2)/c_2$  with a slope of  $-1/k$  and an intercept of  $\theta_2$ . Equation (7) is most satisfactory for use with the lower values of  $c_2$  and Equation (8) is most satisfactory for the higher values.

Since Equations (7) and (8) contain three constants, experimental values of  $\theta$  for any three compositions are of course necessary and sufficient to determine the constants. The accuracy of determination of the constants will be best when the compositions cover as wide a range as possible. Ideally one should choose the two homopolymers and one value near  $c_2 = 0.5$ . Practical considerations, such as the occurrence of crystallinity<sup>8</sup>, may limit observations on the homopolymers.

Figure 1 shows plots according to the form suggested by Equations (7) and (8) for the copolymers of butadiene and styrene made by emulsion polymerization at 50° C. The experimental points, with one exception, were obtained from length, volume, or specific heat measurements<sup>7</sup> at the National Bureau of Standards on polymers whose compositions were determined by carbon-hydrogen analysis. The glass transition temperature values are given in a chapter in Whitby's<sup>8</sup> book. The value of  $k$ , determined as the slope of the line of positive slope and as the reciprocal of the slope of the line of negative slope, is 0.50. A plot of the corresponding data for copolymers prepared at 5° C also yields a value of  $k = 0.50$ .

Figure 2 shows the agreement between the experimental points and the

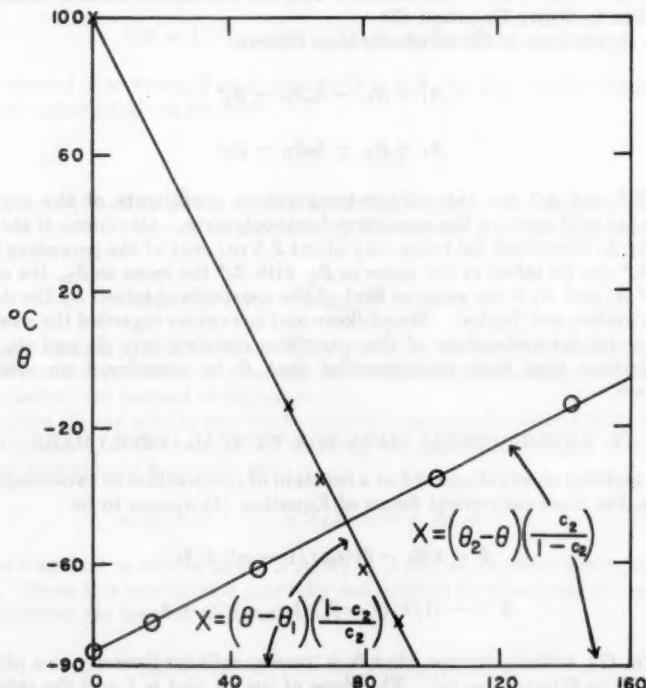


FIG. 1.—Plots suggested by Equations (7) and (8). Copolymers of butadiene and styrene made by emulsion polymerization at 50° C. Data given in reference 8.

curves corresponding to  $k = 0.50$  in a plot of  $\theta$  against composition. The curve for the 50° polymer may be represented by the following equation, obtained by inserting the proper constants in Equation (2):

$$\theta = (-85 + 135c_2)/(1 - 0.5c_2) \quad (9)$$

Correspondingly for the 5° polymer the equation is:

$$\theta = (-78 + 128c_2)/(1 - 0.5c_2) \quad (10)$$

Figure 3 gives the same type of plot as Figure 1 for data recently published by Mandelkern, Martin, and Quinn<sup>8</sup> on vinylidene fluoride and chlorotrifluoroethylene polymers and their copolymers. In this case there was some doubt about the value of the transition temperature for the vinylidene fluoride polymer. Consequently it was first determined from the intercept of the plot of Equation (7) and then used for the plot of Equation (8).

In Figure 4 we have similar plots for data of Loshaek<sup>9</sup> on the copolymers of butyl acrylate and methyl methacrylate.

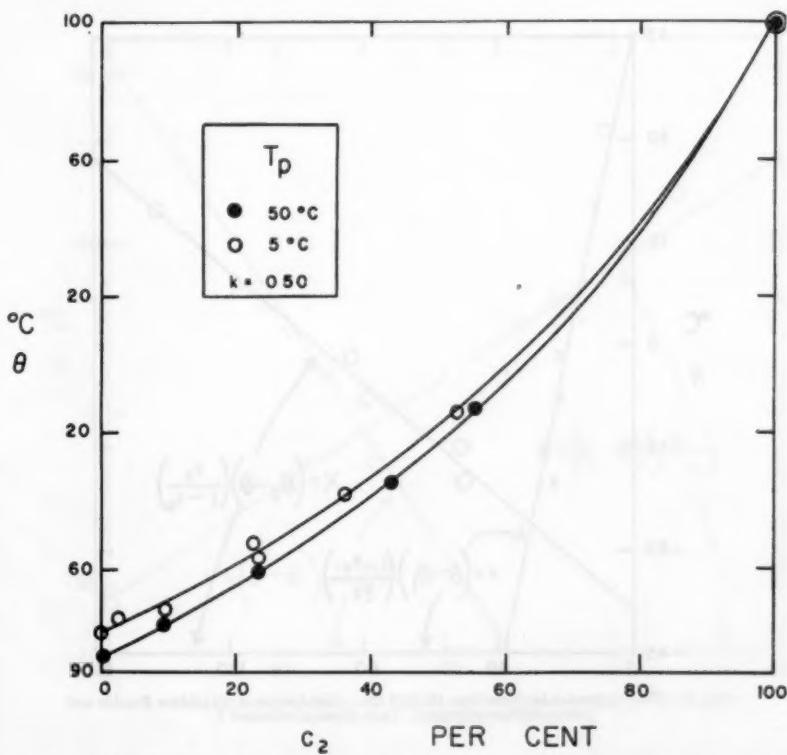


FIG. 2.—Relation of glass transition temperature to composition. Copolymers of butadiene and styrene made by emulsion polymerization at 50 and 5°C. Experimental points represent data given in reference 8.

A number of other copolymer systems have been studied and no instances of systematic deviations from linearity in plots of this type have been noted. We conclude therefore that all available copolymer data can be represented by Equation (1) with  $k = A_2/A_1$  an arbitrary constant for each system. This conclusion is not surprising in view of the fact that Equation (1) can be obtained by several different derivations and that its form is perhaps the simplest one possible for a nonlinear interpolation between the values for the homopolymers. However, the equation does indicate that the glass transition temperature is a

monotonic function of composition and that there is no possibility of a situation analogous to a eutectic mixture.

A different form of equation is required for polymer-plasticizer systems according to Jenckel and Heusch<sup>10</sup>, who present evidence based on studies of various polystyrene-plasticizer mixtures. Equation (1) does not give a satisfactory representation of their results, particularly in the region of high concentration of plasticizer. They also show by direct measurement that for some polymer-plasticizer systems the partial specific volumes are not constant.

Table I shows for various homopolymers the reported values of glass transition

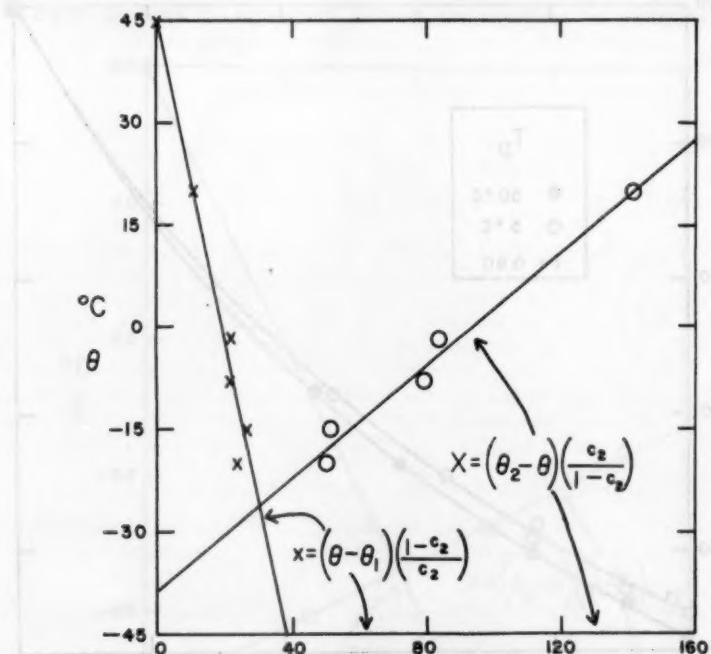


FIG. 3.—Plots suggested by Equations (7) and (8). Copolymers of vinylidene fluoride and chlorotrifluoroethylene. Data given in reference 3.

transition temperature  $\theta$ , volume-temperature coefficient in the rubbery state  $\beta_r$ , volume temperature coefficient in the glassy state  $\beta_g$ , their difference  $\Delta\beta$ , and the product  $\theta\Delta\beta$  with  $\theta$  in degrees Kelvin.

Table II summarizes results obtained for 10 copolymer systems. The values of  $\Delta\beta$  were taken from Table I and the values of  $k$  were determined from the slopes of linear plots like Figures 1, 3, and 4. It can be seen that the observed value of  $k$ , with but two exceptions, is smaller than the ratio of values of  $\Delta\beta$ . Only in the butadiene-styrene system is there approximate agreement.

This lack of agreement is indicative of a deviation from the assumptions made in the derivations of Gordon and Taylor<sup>3</sup> and Mandelkern and coworkers<sup>2</sup>. It is open to question whether one can identify partial specific volumes in

general with the specific volumes of the homopolymers. For the butadiene-styrene copolymers there is experimental evidence<sup>3,11</sup> that this identification is reasonably accurate, and this is indeed the case where  $\Delta\beta_2/\Delta\beta_1$  is nearest the observed value of  $k$ . Similar evidence is not available for the other systems. The assumption<sup>2</sup> that the volume-temperature coefficients for the two components remain the same in the copolymer as in the homopolymers likewise has had no experimental confirmation. The volume-temperature coefficient  $\beta^*$  of the occupied volume entering into the other derivation<sup>3</sup> had not yet been experimentally determined.

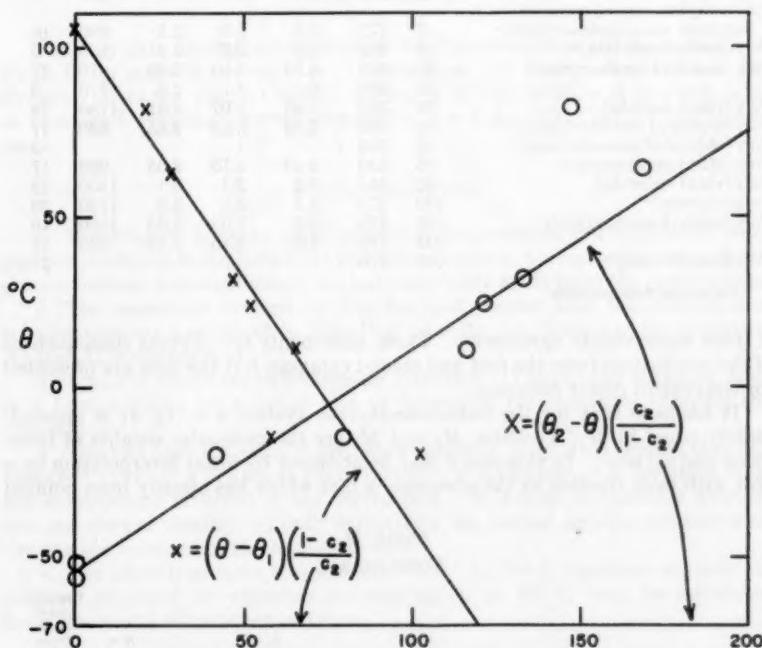


FIG. 4.—Plots suggested by Equations (7) and (8). Copolymers of butyl acrylate and methyl methacrylate. Data given in reference 9.

Since the values of  $k$ , with two exceptions, are less than unity, all the curves of  $\theta$  against weight fraction will, with these exceptions, be convex towards the axis of abscissas (as illustrated by Figure 2).

The third and fourth columns of Table II show the results obtained when the values in the first and second columns are multiplied by  $\theta_2/\theta_1$  in degrees Kelvin. Only in the butadiene-styrene system is the value of  $R = (\theta_2/\theta_1)k$  approximately unity as required in Equation (4) proposed by Fox<sup>4</sup>. However, it appears that the values of  $R$ , on the average, are nearer unity than the values of  $k$ .

It can be seen that the observed value of  $R$  is, with but two exceptions, smaller than the ratio of values of  $\theta\Delta\beta$ . Only in the butadiene-styrene system

TABLE I  
HOMOPOLYMERS

	°C	θ	°K	$\frac{\beta_r}{10^{-4}}$	$\frac{\beta_g}{10^{-4}}$	$\frac{\Delta\beta}{10^{-4}}$	$\frac{\theta\Delta\beta}{10^{-4}}$	Reference
Silicone rubber	-123	150	12	2.7	9.3	1400	13	
Polybutadiene (50°) <sup>a</sup>	-85	188	7.8	2	5.8	1090	8	14
Natural rubber	-72	201	6.16	2.07	4.00	820	15	
Poly(butyl acrylate) <sup>a</sup>	-56	217	6.0	2.6	3.4	740	9	
Poly(vinylidene fluoride) <sup>a</sup>	-39	234						3
Poly(ethyl acrylate) <sup>a</sup>	-22	251	6.1	2.8	3.3	830	9	
Poly(ethylene glycol monoisobutyrate monomethacrylate) <sup>a</sup>	2	275	5.5	3.0	2.5	690	16	
Poly(methyl acrylate) <sup>a</sup>	9	282	5.6	2.7	2.9	820	9	
Poly( <i>n</i> -butyl methacrylate)	20	293	6.10	3.80	2.30	670	17	
	22	295	6.3	3.7	2.6	770	9	
Poly(vinyl acetate)	29	302	5.98	2.07	3.91	1180	18	
Poly( <i>n</i> -propyl methacrylate)	35	308	5.80	3.51	2.65	820	17	
Poly(chlorotrifluoroethylene) <sup>a</sup>	45	318		1				3
Poly(ethyl methacrylate)	65	338	5.40	2.75	2.65	900	17	
Poly(vinyl chloride)	82	355	5.2	2.1	3.1	1100	19	
Poly(styrene) <sup>a</sup>	100	373	5.5	2.5	3.0	1120	20	
Poly(methyl methacrylate) <sup>a</sup>	105	378	5.0	1.95	3.05	1150	16	
	105	378	4.6	2.15	2.45	930	17	
Poly(acrylic acid) <sup>a</sup>	106	379						21

<sup>a</sup> Copolymer data available.

is there approximate agreement. These statements are obvious consequences of the conclusions from the first and second columns, but the data are presented for convenient direct reference.

It happens that for the butadiene-styrene system  $k = A_2/A_1$  is approximately equal to  $M_1/M_2$  where  $M_1$  and  $M_2$  are the molecular weights of butadiene and styrene. In this case  $\theta$  may be obtained by linear interpolation on a plot with mole fraction as the abscissa—a fact which has already been pointed

TABLE II  
COPOLYMERS

Monomer	Comonomer	$\frac{\Delta\beta_2}{\Delta\beta_1}$	$k_{\text{obs}}$	$\theta_2\Delta\beta_2/\theta_1\Delta\beta_1$	$R = \frac{\theta_2}{(\theta_2/\theta_1)k}$	Copolymer data from reference
Butadiene	Methyl acrylate	0.50	0.73	0.75	1.08	22
	Styrene	0.52	0.50	1.03	0.99	8
Butyl acrylate	Styrene	0.88	0.68	1.51	1.16	9
	Methyl methacrylate	0.90	0.66	1.55	1.14	9
Vinylidene fluoride	Chlorotrifluoroethylene	—	0.42	—	0.57	3
Ethyl acrylate	Methyl methacrylate	0.92	0.54	1.39	0.82	9
Ethylene glycol monoisobutyrate monomethacrylate	Methyl methacrylate	1.22	1.32	1.67	1.81	16
	Styrene	1.03	0.56	1.37	0.72	23
	Methyl methacrylate	1.05	0.57	1.40	0.76	9
Methyl acrylate	Acrylic acid	—	1.51	—	2.08	21

out by Catsiff and Tobolsky<sup>12</sup>. Since  $k$  does not turn out to be equal to the ratio of molecular weights for any of the other systems, the relationship for the butadiene-styrene systems must be regarded as fortuitous.

If  $k_{i,j}$  is determined by the ratio of values  $A_j/A_i$  of some property for each homopolymer, and  $A_i$ —whatever its physical significance—is maintained constant in different copolymers, then  $k_{1,2} = A_2/A_1$ ,  $k_{2,3} = A_3/A_2$  and  $k_{1,3} = A_3/A_1$  and thus

$$k_{1,3} = k_{1,2}k_{2,3} \quad (11)$$

Correspondingly

$$R_{1,3} = R_{1,2}R_{2,3} \quad (12)$$

The only data available for a triad with all combinations are those shown in Table II for pairs of polymers of (1) butadiene, (2) methyl acrylate, and (3) styrene. Here the product of  $k_{1,2}$  and  $k_{2,3}$  is  $(0.735)(0.56) = 0.41$  which is to be compared with the directly observed  $k_{1,3} = 0.50$ . This is only fair agreement.

#### V. CONCLUSIONS

1. The relation between glass transition temperature and copolymer composition conforms to Equation (1) and corresponds to a weighted average of the glass transition temperatures of the homopolymers made from the constituents.
2. The equations derived by Gordon and Taylor and Mandelkern and collaborators are equivalent to Equation (1) if the significance of the constants  $A_1$  and  $A_2$  is disregarded.
3. A pair of equations equivalent to Equation (1) have been obtained, each in a form suitable for a linear plot to determine the constants entering the equation.
4. The fact that the ratio of predicted values of  $A_2$  to  $A_1$  is greater than the observed value of  $k$  in almost every instance is indicative of a deviation from the assumptions involved in the derivations. It is open to question whether one can always identify, as both derivations do, partial specific volumes with the specific volumes of the homopolymers.
5. The glass transition temperature  $\theta$  (in ° C) for a butadiene-styrene copolymer prepared by emulsion polymerization at 50° C may be calculated from the bound styrene content  $c_2$  as

$$\theta = (-85 + 135c_2)/(1 - 0.5c_2)$$

and for a similar copolymer prepared at 5° C as

$$\theta = (-78 + 128c_2)/(1 - 0.5c_2)$$

The need for some additional work in this field is obvious. The particular need is for data on specific volume, expansivity, and glass transition temperature for copolymers of accurately determined composition. Only for the butadiene-styrene system are the available data reasonably good, and it is not at all certain how general are the conclusions drawn from this system.

The present work has outlined the methods that may be applied to treat the data when they become available.

## SYNOPSIS

The Gordon-Taylor equation relating the glass transition temperature  $\theta$  of a copolymer to the glass transition temperatures  $\theta_1$  and  $\theta_2$  of the homopolymers is equivalent to

$$A_1 c_1 (\theta - \theta_1) + A_2 c_2 (\theta - \theta_2) = 0$$

where  $c_1$  and  $c_2$  are the weight fractions of the constituents and  $A_1$  and  $A_2$  are constants. It can be recast into the following forms suitable for linear plots

$$\theta = k(\theta_2 - \theta)(c_2/c_1) + \theta_1$$

and

$$\theta = -(1/k)(\theta - \theta_1)(c_1/c_2) + \theta_2$$

where  $k = A_2/A_1$ . Data from the literature on 10 copolymer systems, including butadiene-styrene copolymers, give linear plots, verifying the equation within experimental error. However, the observed value of  $k$  is in most cases significantly smaller than the ratio of the differences of the volume-temperature coefficients for each homopolymer in the rubbery and glassy states, as required by the derivation of Gordon and Taylor. The glass transition temperature (in °C) for a butadiene-styrene copolymer prepared by emulsion polymerization at 50° C may be calculated from the weight fraction  $c_2$  of bound styrene as

$$\theta = (-85 + 135c_2)/(1 - 0.5c_2)$$

and for a similar 5° copolymer as

$$\theta = (-78 + 128c_2)/(1 - 0.5c_2)$$

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# SOME PROPERTIES OF POLYMER NETWORKS FORMED FROM ORIENTED CHAINS OF NATURAL RUBBER \*

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## INTRODUCTION

A three-dimensional polymer network can be formed from an assemblage of individual polymer chains by the intermolecular linking of a sufficient number of chain elements. This intermolecular linking process is termed crosslinking and can be carried out by a variety of chemical methods and in favorable cases by the use of high energy radiation. The network that is formed differs in many of its properties from the original system of polymer chains. A polymer network is characterized by its insolubility, although it has the ability to imbibe many times its volume of liquid when immersed in a good solvent. A non-network collection of polymer chains, on the other hand, will completely dissolve under the same conditions. In the absence of crystallinity a polymer network is also characterized by its long range elasticity at temperatures above its glass temperature. Thus a network has the capacity to support a relatively large stress and to return to its original dimensions when the stress is removed.

In considering the physical and mechanical properties of polymeric networks, from both theoretical<sup>1</sup> and experimental<sup>2</sup> points of view, it always has been assumed that the crosslinking is a random process, i.e., units of different molecules are paired together in an uncoordinated and random manner, and furthermore that the polymer chains are in a randomly coiled configuration. The requirement that chain segments be randomly disposed prior to network formation is obviously a stringent limitation on the types of networks that can be formed. It is well known, for example, that many of the fibrous proteins occur naturally in a state of high orientation and crosslinks if not already present can be introduced without disrupting the characteristic order of the system. Similarly, by a suitable mechanical and thermal treatment many of the more flexible chain-type molecules can be brought to states of high order and orientation and subsequently crosslinked. In a recent theoretical paper Flory<sup>3</sup> has considered the problem of how the properties of a network will depend on the relative arrangement of the chains prior to network formation. In this very general treatment the previous results for the more usual type network are deduced as a special case. The other extreme that can be conveniently considered is the case where the chains are perfectly axially oriented. It was found<sup>4</sup> that the properties to be expected in a network depend not only on the fraction of the units that are randomly crosslinked but also, in a significant manner, on the disposition of the chains prior to network formation. These theoretical deductions are important in efforts to explain the behavior and physical

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properties of both protein and nonprotein macromolecular systems, and it is therefore of interest to assess, by experimental studies, their general validity.

The present paper is concerned with an investigation and comparison of the properties of two types of natural rubber networks. One type of network is the usual type which is obtained when the chains are randomly coiled prior to crosslinking. The other type of network, which has not been heretofore studied, is that formed from chains originally in a highly axially oriented state. Natural rubber was selected for this initial study since it can be crosslinked easily by the action of  $\gamma$ -rays and a great deal of physico-chemical information concerning this polymer is available. The physical properties of the network selected for study were the isotropic melting temperature, the isotropic length and the equilibrium swelling ratio. The manner in which these properties depend on the fraction of the units crosslinked and the mode of network formation were investigated. A preliminary report, which discussed the changes that occur in the isotropic length of a network when it is crosslinked already has been communicated<sup>4</sup>.

## EXPERIMENTAL

**Materials.**—The natural rubber used in this work was obtained from the original latex which contained ammonia as a preservative. Films ranging in thickness from 0.5 to 2.0 mm were prepared in the conventional manner by casting the latex on clean glass plates and allowing it to air-dry for 15 days, during which time the sheet was turned over once or twice to expose both surfaces to air. As would be expected<sup>5</sup> films prepared in this manner were not completely soluble in good solvents such as benzene or toluene, even at elevated temperatures. About 35% of the polymer film thus prepared was found to be insoluble. When immersed in benzene the insoluble gel portion swells to about sixty times its original volume, indicating that the fraction of the units crosslinked is relatively small. However, since the slight amount of crosslinking that is present is a very desirable feature in the subsequent treatment of the film, no effort was made to remove or prevent the formation of gel. The density of the dried latex film was determined by the method of hydrostatic weighings<sup>6</sup> and found to be 0.910 g/cc at 25° which is in accord with the accepted value for natural rubber in the amorphous state<sup>7</sup>. There was no evidence of orientation or crystallization in these films as determined by x-ray diffraction. This material was then used to prepare networks of the type whose chains were in the randomly coiled configuration and also served as the starting material for preparing the highly oriented systems.

**Racking process.**—The highly oriented state of the rubber molecules was obtained by a modification of the "racking process" originally developed and described by Feuchter<sup>8</sup>. The term racked is applied to a polymer sample stretched well beyond its normal limit of extensibility and being capable of maintaining this state without the application of any external force. In this procedure a narrow strip of the latex film is subjected to a very rapid elongation while being held at an elevated temperature and is then quickly cooled to about 20°. Crystallization ensues rapidly at the lower temperature and, when the external force is removed, the specimen remains in the crystalline and elongated condition. By successively repeating the heating, stretching and cooling operations enormous extensions can be reached with natural rubber, elongations as high as 10,000% being reported<sup>9</sup>. However, it is found that the ratio of the extended or racked length to the retracted length of the specimen continually

decreases with each successive racking operation, the maximum in this ratio being achieved after the first step. It appears that continually racking the sample introduces irrecoverable increases in length which may be attributed to such processes as chain rupture or flow. Because of these considerations the oriented samples prepared for study were limited to only one racking cycle.

The maximum extended length that could be attained in one cycle is also strongly influenced by the temperature at which the stretching takes place. For the natural rubber latex films that were used here the optimum temperature was found to be 80°, and a maximum ratio of racked length to retracted length of about eleven was achieved in the specimens used. Extensions of this order are much larger than that usually achieved by subjecting natural rubber to a simple tensile force. Solubility studies indicate that during the one-cycle racking process no change occurred in the proportion of the material that was gel. These high extensions could be obtained by us only when the lightly cross-linked latex film was used. Attempts at racking rubber from other sources as smoked sheet and pale crepe were not nearly as successful. It would appear that a necessary requirement for obtaining high elongation is that the polymer be either lightly crosslinked or be of very high molecular weight.

The wide-angle x-ray pattern of the racked rubber<sup>9</sup> is a characteristic fiber-type diagram with a large number of sharp reflections indicative of high axial orientation. However, an amorphous halo still persists. This latter observation is in accord with our measured density of 0.938 g/cc for the racked rubber, which indicates that though highly oriented only about 35% of the material is in the crystalline state<sup>10</sup>. The highly oriented condition of racked rubber is maintained without the application of any external force at temperatures up to and including 42°. At this temperature the rubber shrinks very quickly to its original length and reverts to the disordered state. Both the original latex rubber and the racked specimens can be crosslinked when exposed to the action of  $\gamma$ -rays from a Co<sup>60</sup> source. As the density of crosslinks in the oriented material is increased, the temperature at which retraction occurs decreases progressively until a point is reached where the samples will retract at room temperature while being irradiated. Despite this limitation on the amount of crosslinking that can be introduced into racked rubber, a sufficient fraction of the units can be interlinked without significant shrinkage occurring, so that the properties of interest and their dependence on crosslinking can be studied.

*Crosslinking procedure.*—Both a 50-curie and a 200-curie Co<sup>60</sup> source located at the National Bureau of Standards were used for the irradiations. The specimens being irradiated were contained in a sealed and evacuated 20-mm Pyrex tube, the flat bottom of which was placed a fixed distance above the source. Prior to being subjected to the action of the  $\gamma$ -rays each strip of racked rubber was split in half along the longitudinal direction, and one of the halves, which served as a control for the length measurements, was not irradiated. The strips to be irradiated were wrapped into coils to fit the inner diameter of the Pyrex tube, and alternate layers of the amorphous unoriented rubber and the racked coils were placed in the tube, and the distance of each sample from the bottom of the tube was noted. The number of samples in a given tube usually ranged from six to ten, and the tube and its contents were subjected to the action of the  $\gamma$ -rays for a predetermined time. Exposure times for the experiments reported here ranged from 6 to 1000 hr. The appropriate dose rate for each sample was determined from its distance from the bottom of the tube, the distance of the bottom of the tube from the source and a previous calibration<sup>11</sup> relating dose

rate and distance from the source. Thus, for a given total exposure time for the entire tube, each sample can be characterized by an equivalent exposure time which is proportional to the radiation dose received. In a typical experiment, if the total exposure time of the tube was 600 hr, the equivalent exposure time of the individual rubber specimen would range from 600 hr to about 100 hr.

*Length measurements.*—Subsequent to the introduction of the crosslinkages each of the racked samples and its corresponding control was immersed in boiling water for a half minute. The shrinkage of both specimens occurred very rapidly under these conditions. The specimens were dried in air for 24 hr at 25° and the lengths measured using a scale which could be read to 0.1 mm. The noncrosslinked control specimens always returned to approximately their original length, which was of the order of one centimeter. This length, characteristic of the material which had been racked but had not been crosslinked, is designated as  $L_0$ . A maximum increase of length due to the racking process itself of about 5% was observed. To minimize the effect that any slow relaxation processes might have, the lengths of the specimens which had been cross-linked in the oriented condition were redetermined after swelling in benzene and redrying *in vacuo*. This length, characteristic of the retracted material which had been crosslinked in the oriented state, is designated as  $L_i$ . In the subsequent discussion, in order to account for the slight increase in length caused by the racking process itself, the ratio  $L_i/L_0$  for each specimen will be considered.

*Sol-gel ratio and equilibrium swellings.*—To determine the fraction of the material partitioned between the sol and gel portions after irradiation, the original unoriented samples and the retracted oriented samples were weighed and immersed in freshly distilled benzene at 25°. Swelling occurred during this process as well as dissolution of the sol fraction. The benzene was replaced every 48 hr and this process was continued for five to ten days. After this period of extraction it was found that the dried insoluble or gel portion had attained a constant weight which did not change on further extraction. To assess the reliability of this method in a few experiments, the total benzene supernatant was evaporated to dryness and the amount of soluble material determined. It was found that the total weight of the sol and the gel portion agreed with the original weight of the material to within 1%. The fraction of sol in these studies ranged from 0.65 for the original material to 0.015 for the most highly irradiated specimens.

After the sol portion had been extracted, the dried and weighed gel was reimmersed in a closed tube containing a large excess of benzene, and the system was thermostated in a water-bath maintained at  $25 \pm 0.1^\circ$ . Preliminary experiments indicated that the swelling equilibrium was attained in seven days since no significant change of weight occurred in the swollen system after this time. After the establishment of equilibrium, the swollen gel was transferred to a weighing bottle and the contents weighed after the liquid adhering to the polymer surface was removed by brief contact with paper. The equilibrium swelling ratio of the network, which is defined as the ratio of the volume of the swollen network to the volume of the dry network, was computed from the above weight, the weight of the dried gel, and the known densities of natural rubber and benzene at 25°.

It must be emphasized that in order to obtain swelling equilibrium measurements that are of physical significance it is mandatory that all the sol be removed from the sample. Besides the obvious correction to the weight of the system that must be made if sol is present, a small amount of soluble polymeric

material will drastically alter the chemical potential of the swelling liquid. Since the equations governing swelling equilibria, particularly the relation between swelling ratio and the fraction of the units crosslinked, are derived on the basis of the swelling in a pure liquid, corrections would have to be applied. The necessary corrections are difficult to introduce in a general way and would require an independent thermodynamic study. The error involved when the above-mentioned precaution is not taken can be quite serious and leads in some cases to an apparent increase in the swelling ratio as the fraction of the units crosslinked increases<sup>12</sup>.

*Melting point determination.*—Following the determination of the equilibrium swelling ratio the dried gel portions were placed in small stoppered tubes and the tubes were maintained at temperatures ranging from  $-18^{\circ}$  to  $-36^{\circ}$  for several weeks. Under these conditions of storage the crystallization of both types of polymer networks ensued, as evidenced by the development of turbidity and loss of the characteristic rubberlike elasticity. After the development of an adequate amount of crystallinity the tubes were heated at the rate of  $3-4^{\circ}$  per hour, and the temperature at which the sample became transparent was taken as the melting point. This temperature could be determined reproducibly to within  $1^{\circ}$ . The relatively rapid heating rate employed<sup>10,13</sup> is not conducive to the formation of the most stable crystallites, and hence this type of observation does not allow the determination of the equilibrium melting temperature. However, this procedure should be adequate for comparing the melting temperature of the different type networks. For present purposes the determination of the relative melting temperatures is all that is required.

## RESULTS AND DISCUSSION

*The crosslinking process.*—In order to describe adequately the determination of the fraction of units crosslinked in each type of network, it will be necessary to discuss briefly the theory of crosslinking and gel formation in polymers. When polymer materials are subject to the effect of high-energy radiation, either crosslinking or chain scission reactions or both usually occur<sup>14,15</sup>. In the case of natural rubber, Charlesby and Groves<sup>12</sup> have demonstrated that the predominant effect is crosslinking and the amount of chain fracture that occurs is very small. When the units of a polymer are crosslinked at random, regardless of the mechanism of the crosslinking process, Flory<sup>16</sup> and Stockmayer<sup>17</sup> have shown that certain critical conditions must be fulfilled in order for gelation to occur. They have shown that for any initial molecular weight distribution, gelation will occur when the fraction of the units in the entire system that are crosslinked  $\rho_1$  is equal to the reciprocal of the weight-average degree of polymerization. The further introduction of additional crosslinks after the gel point has been reached will cause a systematic decrease in the fraction of the polymer that is soluble. In the absence of chain scission reactions, a point eventually will be reached where a sufficient number of crosslinks have been introduced to render the whole material insoluble. However, if the crosslinking is accompanied by chain scission processes then complete insolubility of the material will not be attained.

A quantitative description of the partitioning of the polymer material between sol and gel in the post gelation region has been given by Flory<sup>18</sup> in 1947. Under the assumptions that chain units are paired at random and that chain

scission reactions are absent, he found that the fraction sol of the material  $W_s$ , can be expressed as

$$W_s = \sum_{y=1}^{\infty} w_y [1 - \rho_t (1 - \phi_s)]^y \quad (1)$$

where  $w_y$  is the weight fraction of chains in the original polymer consisting of  $y$  repeating units, and  $\phi_s$  is the probability that a noncrosslinked chain unit selected at random will be part of the sol. This equation is valid for any initial molecular weight distribution of the primary molecules.  $\phi_s$  can be related to  $W_s$  by the relation

$$W_s/\phi_s = 1 - \rho_t (1 - \phi_s) \quad (2)$$

When  $\rho_t$  is small,  $\phi_s$  in Equation (1) can, with negligible error, be identified with  $W_s$ , and the equation reduces to the more useful form of

$$W_s = \sum_{y=1}^{\infty} w_y [1 - \rho_t W_s]^y \quad (3)$$

where  $W_s$  is the weight fraction of the gel.

With the recent renewed interest in crosslinking processes in polymers, due to the availability of high energy radiation sources, Equation (3) has been rederived by Baskett<sup>19</sup>, and an approximate version also has been given by Charlesby<sup>20</sup>. Equations (1) and (2) or their approximate version Equation (3) indicate how the primary molecular weight distribution, characterized by  $w_y$ , can be obtained from a knowledge of the dependence of the sol-gel ratio on the fraction of the units crosslinked<sup>18</sup>. Flory<sup>18</sup> has also shown that for low values of  $\rho_t$  the fraction of the units in the sol that are crosslinked  $\rho'$

$$\rho' = \rho_t W_s \quad (4)$$

while  $\rho$ , the fraction of the units in the gel that are crosslinked, can be expressed approximately as

$$\rho = \rho_t (1 + W_s) \quad (5)$$

In order to apply these considerations to situations where chain scission processes occur concurrently with crosslinking, as often happens when the sample is exposed to high energy radiation, it is only necessary to specify the change that occurs in  $w_y$  as a consequence of the degradation process. For many types of initial distribution the new distribution that results from the random fraction of a given number of bonds can be computed<sup>21</sup>. If the above conditions prevail and the number of fractures is proportional to the radiation dose, the distribution consistent with a given radiation dose, in the absence of crosslinking, can be specified. Similarly if  $\rho_t$  is also proportional to the radiation dose, the fraction sol can be expressed in terms of the radiation dose and the two above-mentioned proportionality factors. Charlesby<sup>20</sup> has considered in detail the situation where a polymer subject to high energy irradiation initially possesses a "most probable" molecular weight distribution, and the number of crosslinks introduced and the number of bonds broken are each proportional to the radiation dose. He found that the manner in which  $W_s$  varies with radiation dose will depend very markedly on the ratio of the number of bonds

broken to the number of crosslinks formed per unit dose. The limiting value of  $W_s$  at high radiation dose reflects the magnitude of this ratio for this type of initial molecular weight distribution. Qualitatively similar results should be expected for other types of initial molecular weight distributions.

In the present work very lightly crosslinked chains in either the disoriented or racked condition were further crosslinked by the action of  $\gamma$ -rays. To study adequately and compare the properties of the resulting networks, it is required that the fraction of the units in the gel that are crosslinked  $\rho$  be specified. This quantity, for the networks formed from disoriented chains, can be obtained in a relatively simple manner from the equilibrium swelling ratio in a suitably chosen solvent by use of the conventional swelling equations<sup>22,23</sup>. Unfortunately this procedure is not directly applicable to networks formed from highly oriented chains (see discussion of swelling below) since the appropriate swelling equation contains a parameter which depends on the disposition of the chains prior to crosslinking and this parameter has not as yet been susceptible to calculation.

In order to circumvent this difficulty, advantage can be taken of the fact that in a series of experiments it was found that for both the disoriented chains and the racked chains the limiting value of  $W_s$  ranges between 0.015 to 0.020. Thus following Charlesby's analysis we can conclude that the ratio of the number of bonds broken to the number of crosslinks formed per unit radiation dose is the same in the two cases and that the crosslinking process is by far the predominant effect. Since both types of chains possess the same initial molecular weight distribution, the variation of  $W_s$  with radiation dose should be identical in the two cases provided only that the same proportionality exists between  $\rho_t$  and radiation dose. If, however, the above-mentioned proportionality is different in the two cases, then the fraction of sol will not be the same at a given radiation dose. From any observed differences that may occur in the fraction of sol, the relative amounts of crosslinking in the two cases can be deduced. Since for the network formed from random chains an absolute value of  $\rho$  can be obtained from swelling equilibrium and  $\rho_t$  obtained by application of Equation (5), knowledge of the relative efficiency of crosslinking will enable  $\rho_t$  to be determined from the network formed from ordered chains.

To evaluate the relative efficiencies of the crosslinking process, the fraction sol of each type of network was determined at various radiation dosages so chosen that  $W_s$  ranged from 0.65 to 0.20. The results of these experiments are illustrated in Figure 1, where the sol fraction is plotted against radiation dose, the dosage being expressed in terms of the equivalent time of exposure. The solid curve is drawn through the experimentally observed points representing the results for crosslinking chains in the highly oriented state, while the open circles represent the fraction sol obtained when the random chains were cross-linked. Under corresponding conditions the fraction sol obtained from the oriented chains is always less than when the chains are arranged at random. Since chain scission processes are small and in the same proportion to cross-linking in both cases the plot in Figure 1 indicates that for any given radiation dose crosslinking is more effective in the racked system. The dashed curve in this plot is obtained from the solid curve by multiplying the abscissa corresponding to a given  $W_s$  by a factor of two. The dotted curve adequately represents the data for the networks formed from the collection of randomly coiled chains. It can thus be concluded that the crosslinking of the racked chains is about twice as efficient as the crosslinking of the chains in the disordered state.

The above analysis is probably an underestimate of the relative crosslinking

efficiencies of the two cases since in highly oriented systems a greater proportion of crosslinks will be between adjacent chains already crosslinked and part of the gel. Crosslinks of this type will not be effective in causing additional molecules to become part of the gel and can be considered to be wasted crosslinks. This effect should become more pronounced at low fraction of sol and should not seriously affect the above analysis which is limited to higher sol concentrations. The reasons for the large differences in the relative efficiencies of crosslinking in

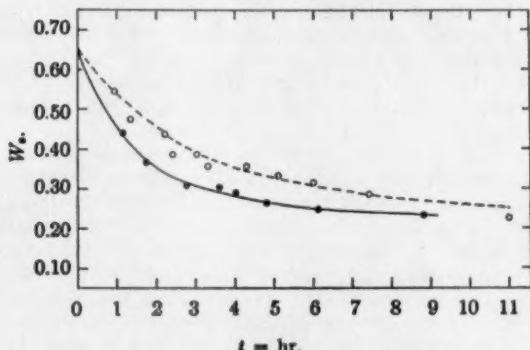


FIG. 1.—Fraction of sol,  $W_s$ , versus equivalent irradiation time,  $t$ : racked rubber, ●; amorphous rubber, ○.

the two cases is not readily understood, nor is it clear as to whether it is due to the crystallization, the orientation or a combination of both. Though these observations are of significance in themselves, the problem has not as yet been investigated any further since it is not pertinent to the present investigation.

*Swelling behavior.*—The theoretical relation derived by Flory<sup>3</sup> which describes the swelling equilibrium of a polymer network can be expressed as

$$[V_1\rho/\bar{v}M_0][\langle\alpha\rangle_0^2v_2^{\frac{1}{2}} - v_2/2] = - [\ln(1 - v_2) + v_2 + \chi_1v_2^2] \quad (6)$$

where  $v_2$  is the volume fraction of polymer in the swollen gel, i.e., the reciprocal of the equilibrium swelling ratio  $Q_m$ ,  $V_1$  and  $\bar{v}$  are the molar volume of the swelling liquid and specific volume of the polymer, respectively,  $M_0$  is the molecular weight of the chain repeating unit,  $\chi_1$  is the thermodynamic interaction parameter<sup>2</sup> and  $\langle\alpha\rangle_0$  is a parameter which is dependent on the disposition of the polymer chains relative to one another prior to the random introduction of crosslinks.

In considering the properties of a network, where the stipulation is not made that the chains be randomly disposed relative to one another prior to crosslinking, a reference state of the isotropic (zero force) network<sup>3</sup> is taken as that where the mean square components of the chain vectors are equal to each other and consequently equal to one third the mean square end-to-end distance of the unconstrained or free chain  $r_0^2/3$ . Limiting considerations to networks formed at constant temperature and in the absence of diluent the mean square end-to-end distance of the chains for the isotropic network will depend on the relative disposition of the chains prior to network formation. If the mean square end-

to-end distance of the chains in the network in the isotropic state at the same volume of the reference state is  $\bar{r}_i^2$ , then the quantity  $\langle \alpha \rangle_0$  is defined<sup>2</sup> as  $(\bar{r}_i^2/r_0^2)^{1/2}$  and measures the geometric mean of the linear dilation of the network relative to the reference state. For networks formed from chains randomly arranged  $\bar{r}_i^2$  will be equal to  $r_0^2$  and  $\langle \alpha \rangle_0$  will obviously be equal to unity. However, for networks formed from oriented chains the value of  $\langle \alpha \rangle_0$  will depend on the details of chain dimensions and arrangements prior to crosslinking. For highly oriented chain  $\langle \alpha \rangle_0$  has as yet not been susceptible to direct calculation but generally can be expected to differ from unity<sup>3</sup>.

When  $\langle \alpha \rangle_0$  is equal to unity Equation (6) reduces to the conventional or more usual equilibrium swelling relation. The resulting equation then can be used to calculate  $\rho$  for the case of the random crosslinking of random chains as long as  $\chi_1$  can be specified. However, for a network formed by the crosslinking of oriented chains,  $\langle \alpha \rangle_0$  will differ from unity by an unspecified amount. Hence in this case  $\rho$  cannot be determined solely from equilibrium swelling measurements. It is this consequence of Equation (6) which necessitates the adoption of the following procedure in order to determine  $\rho$  for this type network.

It may be recalled that each tube that was irradiated consisted of alternate layers of amorphous unoriented rubber and of racked rubber, and each sample could be characterized by an equivalent radiation time. For the initially amorphous samples in each tube the value of  $\rho_t$  could be determined from the fraction gel and the swelling equilibrium of the gel portion in benzene by use

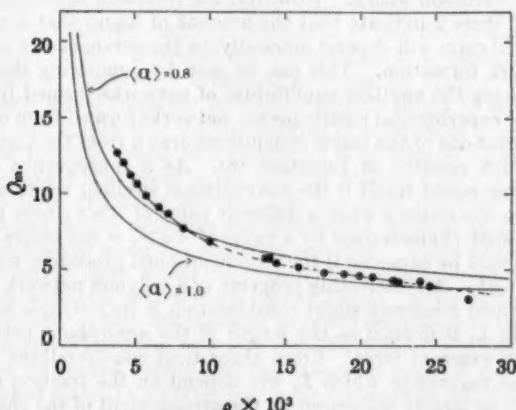


FIG. 2.—Swelling ratio,  $C_r$ , versus fraction of units crosslinked,  $\rho$ . Solid lines are theoretical curves calculated from Equation (6) for indicated values of  $\langle \alpha \rangle_0$ . Experimental results for networks formed from oriented chains designated by ●.

of Equation (6), ( $\langle \alpha \rangle_0 = 1$ ) employing Gee's<sup>24</sup> value of 0.395 for  $\chi_1$ . Though for this type of rubber  $\rho_t$  increased monotonically with the equivalent radiation time an exact direct proportionality between the two quantities was not observed. The value of  $\rho_t$  for an oriented system irradiated for a given equivalent time was obtained by first considering the appropriate value for an amorphous system under the same condition of irradiation. This latter quantity could be

deduced easily by interpolation from the observed results for the amorphous system. The value appropriate to an oriented system at the same equivalent time is obtained when the relative efficiency of crosslinking of the two types of systems is accounted for. This is accomplished when the value of  $\rho_t$  for the amorphous polymer is multiplied by a factor of two. The procedure just outlined was used to determine  $\rho_t$  for the oriented systems. The value of  $\rho$  for the network formed from the oriented chains is then obtained by using Equation (5).

The solid circles plotted in Figure 2 are the experimental results obtained for the equilibrium swelling ratios of the networks obtained from the highly oriented specimens. A large range in crosslinking density is covered by these experiments with a maximum of 3% of the units being involved in crosslinkages. The plotted points delineate a curve indicated by the dashed curve in the figure. The shape of this curve over the complete crosslinking range is such that it cannot be exactly described by Equation (6) with a fixed though arbitrary value of  $\langle \alpha \rangle_0$ . This can be seen by comparing the plotted points with the two solid curves in the plot which were calculated from Equation (6) for values of  $\langle \alpha \rangle_0 = 1.0$  and  $\langle \alpha \rangle_0 = 0.8$ , respectively. The deviations from the theoretical relation are beyond the experimental errors, and if Equation (6) is to apply,  $\langle \alpha \rangle_0$  must vary with  $\rho$ . This possibility already has been considered by Flory<sup>3</sup> in his original consideration of the problem. In order to satisfy the experimental results for this case,  $\langle \alpha \rangle_0$  would have to vary from 0.75 to 1.0 over the crosslinking range.

An exact quantitative comparison between theory and experiment is obviously very difficult to make because of the inherent difficulty of specifying  $\langle \alpha \rangle_0$  and its variation with  $\rho$ . However, the results of these experiments as illustrated in Figure 2 indicate that the amount of liquid that a network will imbibe at equilibrium will depend markedly on the arrangement of the chains prior to network formation. This can be seen by comparing the theoretical curve representing the swelling equilibrium of networks formed from random chains with the experimental results for the networks formed from order chains. This fact confirms one of the major conclusions drawn from the theoretical considerations which resulted in Equation (6). As a consequence of this fact appreciable error would result if the conventional swelling relation ( $\langle \alpha \rangle_0 = 1$ ) were used to determine  $\rho$  when a different value of  $\langle \alpha \rangle_0$  were appropriate. Thus for a network characterized by a value of  $\langle \alpha \rangle_0 = 0.8$  errors of the order of 30 to 50% could be expected if the aforementioned procedure were adopted.

*Isotropic length.*—An interesting property of a polymer network which heretofore has received relatively slight consideration is its isotropic length. The isotropic length  $L_i$  is defined as the length of the amorphous network in the absence of any external force. From theoretical considerations Flory<sup>3</sup> concluded that the manner in which  $L_i$  will depend on the fraction of the units crosslinked will be largely influenced by the arrangement of the chains prior to the introduction of crosslinks. He derived the relation that

$$L_i = (\nu/\sigma')(\bar{r}_0^2/3)^{\frac{1}{2}} \langle \alpha \rangle_0 \quad (7)$$

where  $\nu$  is the number of chains in the network and  $\sigma'$  to a good approximation can be identified with the number of chain vectors passing through a plane transverse to the axis of the sample, it being assumed that the value of  $\sigma'$  at the time of network formation and in the isotropic state are identical.

If a collection of chains in the randomly coiled configuration are crosslinked

then, as defined above, the resultant network will be in the isotropic state regardless of the number of crosslinks introduced. The length of the network would then be  $L_i$ , and except for a very small variation due to the density change that accompanies the actual crosslinking process, would be independent of  $\nu$ . The fact that a Gaussian distribution of chain end-to-end distances is maintained prior to and subsequent to the random crosslinking process requires that this condition be fulfilled. This fact is easily verified experimentally. Since  $r_0^2$  will vary inversely as  $\nu$ , it can be concluded<sup>3</sup> from Equation (7) that for a network formed in this manner  $\sigma'$  must increase as  $\nu^{\frac{1}{2}}$ .

This increase in  $\sigma'$  with crosslinking has been given qualitative explanation<sup>3</sup> by the fact that a plane transverse to the sample axis will be intersected many times by the segments of a given randomly coiled chain. Hence when subsequent crosslinks are introduced, not only are more chain vectors added to the system but more of the vectors will intersect the plane under consideration with the resultant increase in the value of  $\sigma'$ . However, if the polymer chains are oriented prior to the introduction of crosslinks, the number of segments of a given chain which intersect the transverse plane must necessarily decrease. Thus if the same number of new chain vectors are introduced as in the previous case, the number of these vectors which cross the transverse plane will not be as great and consequently  $\sigma'$  will not increase as rapidly with the crosslinking density. In the extreme case of perfect axial orientation  $\sigma'$  will be equal to the number of polymer molecules in a cross section and obviously will then be independent of the amount of crosslinking. Since  $r_0^2$  will vary inversely as  $\sigma'$  we conclude from Equation (7) that for this case  $L_i$  should increase directly as  $\nu^{\frac{1}{2}} < \alpha >_0$ . Thus the two extreme cases of chain arrangements prior to network formation lead to quite different expectations as to how the isotropic length will depend on crosslinking. If perfect axial orientation of a collection of polymer molecules could be achieved, it is implied by Equation (7) that the first crosslinks introduced would cause the isotropic length to shrink to zero.

Since it is well known that the crosslinking of amorphous unoriented chains does not alter the dimensions of a sample, it is of interest to investigate the dimensional changes that occur in the isotropic state of a network formed from chains which were originally oriented. It has been reported<sup>25,26</sup> that when stretched natural rubber networks are crosslinked, there is an increase in the length of the sample when the stress is removed. These experiments were limited, however, to cases where the crosslinks were introduced into deformed systems which were still within the Gaussian range. Systematic quantitative studies, particularly at high orientations, have not been made to test adequately any of the conclusions that can be drawn from Equation (7). The high orientation possessed by racked rubber and the ease with which it can be quantitatively crosslinked make it a suitable polymeric system with which to study these effects.

A brief report on the change of  $L_i$  with crosslinking for racked rubber samples already has been given<sup>4</sup>, and reference is made to the figure contained in that communication. To account for minor variations among the different specimens the ratio of  $L_i$  to  $L_0$  the length of the retracted but noncrosslinked specimen was considered. This ratio increased by a factor of two and a half over the fiftyfold range of crosslinking encompassed by the experiments. When the ratio  $L_i/L_0$  is plotted against  $\rho^{\frac{1}{2}}$ , as in the figure cited<sup>4</sup>, it is found that for values of  $\rho^{\frac{1}{2}}$  greater than  $9 \times 10^{-2}$  the data are well represented by a straight line whose slope is 15. When this straight line is drawn so as to correspond to

lower values of  $\rho^{\frac{1}{2}}$ , it extrapolates almost exactly to the origin. However, the actual experimental results at the lower crosslinking densities show marked deviations from the straight line delineated by the data at the higher crosslinking densities. In fact the ratio  $L_i/L_0$  approaches unity with an almost horizontal slope. Thus we observe that the initial introduction of crosslinks causes only a slight increase in the isotropic length, but after about 1% of the chain units become involved in crosslinkages, the isotropic length increases linearly with  $\rho^{\frac{1}{2}}$ .

In order to consider these experimental results in more detail, it will be convenient to reduce Equation (7) to a form which will be more appropriate for the consideration of networks formed from highly oriented chains. If  $V$  is the volume of the specimen (assumed to be the same in the retracted and the racked state) and  $L_r$  is its length in the racked state, then for perfect axial orientation the number of chains which intersect a plane transverse to the axis of the specimen can be written as

$$\sigma' = V/(L_r a) \quad (8)$$

where  $a$  is the cross sectional area of a single chain. For a system containing  $N_0$  units,  $\nu = N_0\rho$  and since  $(\bar{r}_0^2)^{\frac{1}{2}}$  can be expressed as  $(\bar{r}_0^2/M)^{\frac{1}{2}}(M_0/\rho)^{\frac{1}{2}}$ , Equation (7) becomes

$$L_i/L_0 = (L_r/L_0) \{ [N_a a / (\sqrt{3} M_0^{\frac{1}{2}} \bar{v})] (\bar{r}_0^2/M)^{\frac{1}{2}} \} \rho^{\frac{1}{2}} <\alpha>_0 \quad (9)$$

where  $N_a$  is Avogadro's number. Thus from Equation (9), an estimate can be made of the slope to be expected from the linear plot of  $L_i/L_0$  against  $\rho^{\frac{1}{2}}$ .

The two molecular quantities,  $\bar{r}_0^2/M$  and  $a$ , which are needed to evaluate this slope, are available as a result of the intensive investigations of the properties of natural rubber. From the appropriate dilute solution studies of the configurational properties of natural rubber, Wagner and Flory<sup>27</sup> have concluded that  $(\bar{r}_0^2/M)^{\frac{1}{2}}$  is equal to  $0.83 \times 10^{-8}$  cm. The extensive crystallographic studies of Bunn<sup>28</sup> have resulted in a detailed analysis of the structure and dimensions of the unit cell. From this work the cross sectional area of a chain is found to be  $27.8 \times 10^{-16}$  cm<sup>2</sup>. The specific volume of amorphous natural rubber at 25° is  $1.10 \text{ cm}^3/\text{g}$ <sup>2</sup>, so that the quantity in the braces of Equation (9) becomes equal to 0.89. Since in these experiments the ratio of  $L_r/L_0$  is between eleven and twelve, and an average value of  $<\alpha>_0$  can be taken as 0.9, a theoretical slope of approximately 10 is predicted from Equation (9). This theoretical estimate compares favorably with the value of 15 observed for the linear portion of the plot and gives strong substantiation to the theoretical conclusions. The discrepancy between the theoretical and observed slope can be attributed in part to uncertainties in the value of  $a$  and  $\bar{r}_0^2/M$ , approximations in the theory and the assumed invariance of  $\sigma'$ .

These results show that a substantial increase in the isotropic length of a sample can be accomplished by crosslinking chains in an oriented state. The limitation imposed on the number of crosslinks that can be introduced into racked rubber without retraction occurring already has been discussed. It would appear that if a higher crosslinking density could be accomplished, even larger values of the isotropic length would be attained. This phenomenon is not limited to natural rubber. It appears to be true for crosslinked (tanned) collagen fibers<sup>29</sup>, and preliminary experiments from this laboratory indicate that similar effects, but of greater magnitude, occur when highly oriented polyethylene is crosslinked.

The density values of the racked rubber specimens and the wide-angle x-ray diffraction patterns indicate that though substantial orientation can be achieved by the racking process, the samples are not completely crystalline nor is the orientation perfect. Thus when crosslinks are initially introduced into the system, units of disordered and partially oriented chain units will become cross-linked so that a chain direction may reverse itself several times between cross-links. This would, of course, result in only a slight increase in  $L_i$ . However, at higher degrees of crosslinking, because of the fact that a substantial amount of chain orientation is present, this reversal of chain directions should be decreased. Hence, the number of chain vectors intersecting a given transverse plane should tend to remain constant and one would expect the dependence of  $L_i$  on  $\rho^4$  that is observed. The fact that this straight line extrapolates to the origin would appear to indicate that these conditions hold after about 1% of the chain units are crosslinked.

*Isotropic melting temperature.*—When a homopolymer of sufficiently regular structure as natural rubber is brought to an appropriate temperature, crystallization will ensue without the application of any external stress. X-ray diffraction studies indicate that when the crystallization is induced solely by cooling, the crystallites will be randomly arranged relatively to one another. When adequate care is taken during the subsequent fusion process to ensure that conditions close to equilibrium are maintained, the melting of a homopolymer is very sharp. The melting process under these circumstances can be considered to be thermodynamically reversible, and the last traces of crystallinity disappear at a well defined and reproducible temperature.

On the other hand, if the crystallites in a polymer system are oriented without the maintenance of an equilibrium stress, though at a given temperature a crystal-to-liquid transformation occurs, this temperature is not necessarily one of thermodynamic equilibrium. The nonequilibrium aspects of the fusion of oriented systems (when an equilibrium external force is not applied) was first discussed with respect to the problem of melting of stark rubber<sup>30</sup> and more recently with regard to the shrinkage of racked rubber<sup>31</sup> and the hydrothermal shrinkage of native collagen<sup>32</sup>. Though there are restrictions as to when equilibrium considerations can be applied to the fusion of polymers, it is a legitimate procedure to employ when the crystallization is induced from the melt solely by cooling. It is thus a matter of interest to see how the melting temperature of a network crystallized solely by cooling will depend on the mode of network formation and the concentration of crosslinkages.

As a consequence of the heating rate employed,  $T_m$  for the noncrosslinked rubber was found to be between 9 and 10°, which is appreciably lower than the expected equilibrium melting temperature of 28–30°<sup>10,33</sup>. The experimentally observed melting temperatures of the two different types of networks are illustrated in Figure 3. The upper curve in this plot represents the results for the networks formed from originally oriented chains while the lower curve is for the usual type of network. For both types of networks an appreciable depression of the melting point occurs as the fraction of units crosslinked is increased. This effect is similar in magnitude to that which has been reported previously<sup>34</sup> for the melting of natural rubber networks formed from unoriented chains by chemical methods. For the latter cases the melting temperatures were determined under conditions which should yield the equilibrium melting temperatures. This unexpected result appears to be due solely to the introduction of crosslinks and is independent of the mode of crosslinking. Despite this fact, the data clearly indicate that at all levels of crosslinking the values of  $T_m$  for

the usual type of network is less than the corresponding value for networks formed from oriented chains. These differences range from 1–3° at the smaller values of crosslinking to 9–10° when  $\rho$  equal to  $15 \times 10^{-3}$  and appear to be diverging further at still higher levels of crosslinking. It is significant to note that for the usual type networks having crosslinking values in the range of  $\rho$  equal to  $2-3 \times 10^{-2}$ , no crystallization is detected when these samples are held at  $-36^{\circ}$  for an extended period of time while crystallization ensues relatively rapidly for comparable networks formed from oriented chains. Thus we conclude that the value of  $T_m^i$  depends not only on the fraction of the units crosslinked but also in a significant manner on the arrangement of the chains prior to network formation.

For a network formed from chain units randomly arranged, it might be supposed that the units involved in the crosslinkages will not participate in the

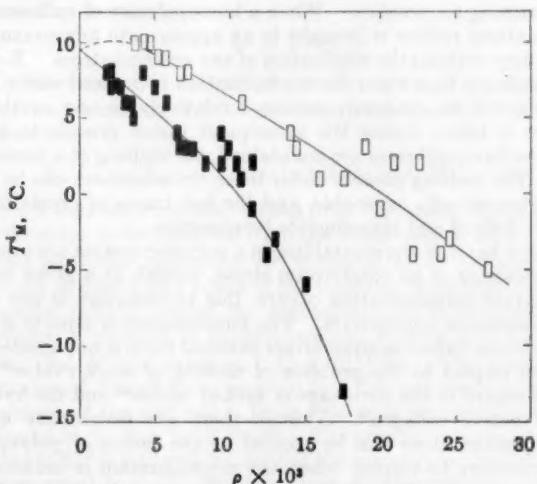


FIG. 3.—Isotropic melting temperature,  $T_m^i$ , versus fraction of units crosslinked,  $\rho$ ; results for networks formed from random chains, ■; results for networks formed from oriented chains, □.

crystallization. The melting temperature would then be expected to be depressed in a manner similar to that which occurs on the random introduction of noncrystallizing copolymeric units to a homopolymer. If this fact were the sole consideration, then for the usual range of crosslinking encountered, melting temperature depressions of only two or three degrees would be expected<sup>23,24</sup>. The experimental results indicate that this is obviously not the case. Though the rather large melting point depression observed on crosslinking has not as yet received a quantitative theoretical explanation, a qualitative hypothesis can be advanced. The relations derived for the melting temperature of random copolymers are based in part on the assumption that since the polymer chains are not tied together in any permanent manner, there are no restrictions applied to the lateral growth of the crystallites which are formed<sup>25–27</sup>. Under equilibrium conditions the longitudinal size of the crystallites would be restricted, however, by the requirements of the copolymer composition. In a net-

work, however, the points of crosslinkage will not only restrict the longitudinal growth, but since portions of chains are permanently tied together unrestricted lateral growth of a crystallite cannot occur. This would appear to be the major difference between the equilibrium crystallization and melting of a network and a random copolymer. For the same composition of extraneous ingredients, i.e., crosslinkages or noncrystallizing copolymeric units, crystallites in a network would be expected to melt at a lower temperature than the corresponding copolymer under equilibrium conditions. The melting point depression would then depend primarily on the fraction of the units crosslinked and only to a lesser extent on the nature of the crosslinking process. This effect should be solely the result of the introduction of crosslinks and should not depend on the relative disposition of the chains prior to crosslinking.

When polymer molecules in the random state are crosslinked no change occurs in the configurational entropy of the individual chains since the units which are paired together are selected at random. Thus the contribution of the configurational entropy in the liquid state to the total entropy of fusion will remain unaltered. However, as Flory<sup>3</sup> has pointed out, the situation is quite different when axially oriented chains are crosslinked. In this case a crosslink must join two adjacent molecules together. Thus if a unit of a given molecule is to be crosslinked to another unit, this latter unit must be in an adjacent position on a neighboring molecule. Even though the crosslinks are distributed at random in space, the crosslinking process does not involve the random selection of pairs of units. The specification of adjacent units of neighboring molecules imposes an order on the system, which will persist in the liquid state because of the permanence of the crosslinks. The configurational entropy of the chains in the liquid state is decreased by this process, and the entropy of fusion will be altered in a corresponding manner. The melting temperature of this type network would then be expected to be larger than that for the non-crosslinked system from which it is formed and also should be greater than the corresponding network formed from random chains. However, this expected increase in  $T_m^i$  on crosslinking oriented chains may be offset by the nonconfigurational effects of the crosslinks which cause a major depression of the melting point. These considerations are in accord with the observed values of  $T_m^i$  for both types of networks.

An exact quantitative comparison between experiment and theory must await a more detailed explanation of the large melting point depression caused by the crosslinking of the random chains as well as the determination of melting temperatures under conditions more closely approaching those of equilibrium. Preliminary calculations utilizing the data of Figure 3 indicate very good accord between the difference in melting temperature of the two types of networks and the theoretical equations<sup>2</sup>.

#### SUMMARY

Highly oriented natural rubber samples prepared by a modification of the racking process described by Feuchter were crosslinked by means of  $\gamma$ -radiation. Some of the physical properties of the networks prepared in this manner were studied and compared with networks formed from chains which were randomly arranged prior to the introduction of the crosslinks. In accord with the theoretical considerations of Flory it was found that the swelling behavior, isotropic length, and isotropic melting temperature of the networks depend not only on the fraction of units crosslinked but also very markedly on the arrange-

ment of the chains prior to network formation. It also was observed that the crystalline oriented racked rubber was crosslinked twice as effectively by  $\gamma$ -radiation as was the amorphous rubber.

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## THERMODYNAMICS OF SHRINKAGE OF FIBROUS (RACKED) RUBBER \*

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Highly oriented, crystalline fibrous proteins display marked contractions when subjected to conditions which induce melting. The dimensional change is particularly striking in the case of native collagen fibers which melt with reduction in length by a factor of about one-fifth. Moreover, the transformation is macroscopically discontinuous, a partially shrunken fiber comprising two distinct regions meeting at a rather well-defined boundary transverse to the fiber axis<sup>1</sup>. One of these regions consists of native fiber, highly birefringent and relatively inextensible under tension; the other region is completely amorphous, nonbirefringent (nearly) and rubberlike. The latter zone is most easily distinguished by its greater width.

In connection with a current series of investigations on the shrinkage and elastic deformation of collagen and related fibrous proteins<sup>1,2</sup>, it seemed desirable to prepare a model system from a random-coiling, long-chain polymer capable of crystallizing when stretched. Inasmuch as collagen becomes rubberlike upon shrinking and natural rubber can be rendered fibrous by severe stretching (racking), natural rubber seemed an appropriate choice. Preliminary samples of racked rubber made available to us by Roberts and Mandelkern<sup>3,4</sup> of the Bureau of Standards revealed a capacity for shrinkage upon heating which is similar in all respects to the shrinkage of collagen, except that a swelling agent (e.g., water in the case of collagen) is not required. Upon heating above the shrinkage temperature (ca. 35° in the absence of tension) nodular regions of amorphous rubber appear between adjoining untransformed zones of racked rubber; the transformation at a given temperature can be arrested by application of tension. The introduction of crosslinks by  $\gamma$ -radiation in the racked state<sup>5</sup> serves to suppress plastic flow upon melting, as is essential for establishment of states of equilibrium. Crosslinking in this manner is analogous to "tanning" of native collagen fibers, which likewise introduces crosslinks in the highly oriented state.

If we regard the coexisting "racked" and amorphous zones as phases, then the tensile force  $f_{eq}$  required to maintain equilibrium between these phases must be related to the temperature according to the analog of the Clapeyron equation<sup>5,6</sup>.

$$(\partial f_{eq}/\partial T)_P = - \Delta S/\Delta L \quad (1)$$

where  $\Delta S$  and  $\Delta L$  are the latent changes in entropy and length associated with

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the transformation of the fiber under the conditions specified by  $T$  and  $P$ . Since at equilibrium between the phases

$$\Delta H - T\Delta S - f\Delta L = 0 \quad (2)$$

it follows that Equation (1) may be replaced by

$$[\partial(f_{eq}/T)/\partial(1/T)]_P = \Delta H/\Delta L \quad (3)$$

where  $\Delta H$  is the latent enthalpy change. Thus, determination of  $f_{eq}$  as a function of  $T$  offers a means for evaluating  $\Delta H$ .

The investigation herein reported was concerned with processes of dimensional change in natural rubber samples crosslinked by exposure in the racked state to  $\gamma$ -radiation. The relationship of stress to strain is examined for both the racked and the totally amorphous (shrunken) states. Principal attention, however, focuses on the equilibrium between coexisting racked and amorphous portions of the sample in the partially shrunken state. A method is described for determining the force  $f_{eq}$  required for equilibrium between these phases, and the thermodynamic relation expressed in alternative forms by Equations (1) and (3) is applied to samples of racked rubber crosslinked to different extents as described in the preceding paper<sup>3</sup>.

## EXPERIMENTAL

*Samples.*—Natural rubber specimens prepared from cast latex films were supplied by Roberts and Mandelkern<sup>3</sup>, whose assistance is gratefully acknowledged. The procedure used to impart high orientation (i.e., racking) is described in the preceding paper<sup>3</sup>. A high degree of orientation was indicated both by the X-ray diffraction pattern and by the approximately elevenfold shrinkage in length upon melting the crystalline racked sample by warming.

Crosslinking was carried out in the racked state by the action of  $\gamma$ -radiation, as described by Roberts and Mandelkern. Three samples were irradiated for the same time (600 hours) *in vacuo* but at different distances from the 50 curie Co<sup>60</sup> source. These are designated b-2, f-1 and l-1 in decreasing order of crosslinking. The range in degree of crosslinking is about twofold (see Table III).

The cross sections of the amorphous, i.e., shrunken, samples were determined under a microscope equipped with a micrometer eyepiece. The cross section in conjunction with the length (under zero force) between the clamps yielded the sample volume. Lengths of the racked samples were 5 to 10 cm; the lengths of the amorphous (shrunken) samples under no force were 1 to 2 cm. Cross sections in the amorphous state were ca.  $7 \times 10^{-3} \text{ cm}^2$ .

*Determination of densities and degrees of crystallinity.*—The densities of samples in the racked and in the amorphous states were determined by comparing the weight *in vacuo* and in methanol at 25°. The quartz spring used for the weighings had a sensitivity of ca. 0.5 mm/mg; the length of the spring was measured with a cathetometer to an accuracy of  $5 \times 10^{-3}$  mm, corresponding to  $10^{-2}$  mg. Using samples of ca. 15 mg, the densities could be determined with an accuracy of ca.  $\pm 0.0005 \text{ g cc}^{-1}$ . Vacuum was applied for the purpose of eliminating gas bubbles from the surface of the sample immersed in methanol prior to weighing.

The densities of the three samples investigated are recorded in Table I. The close agreement between the densities of these samples in the racked state,

as well as in the amorphous state, is not unexpected inasmuch as the same racking procedure was applied to each. The x-ray density of crystalline rubber according to Bunn<sup>7</sup> is  $1.009 (\pm 0.010)$  g cc<sup>-1</sup> at 25°. Assuming that the density increases linearly with the degree of crystallinity, we obtain the results given in the last row of Table I. The values found for the per cent crystallinity are

TABLE I  
SAMPLE DENSITIES (G CC<sup>-1</sup> AT 25°) AND DEGREE OF CRYSTALLINITY

	b-2	f-1	l-1	Av.
Amorphous density	0.9100	0.9102	0.911	0.910
Racked density	0.9346	0.9342	0.934	0.934
% Crystalline	25	24	24	24 ± 2

somewhat lower than the 35 per cent figure obtained by Roberts and Mandelkern<sup>3</sup> for racked samples prior to crosslinking. The difference, if real, suggests a decrease in crystallinity during the crosslinking process.

**Tension Measurements.**—A diagram of the dynamometer is shown in Figure 1. The crystalline, racked sample, 5 to 10 cm in length and ca.  $2 \times 10^{-3}$  cm<sup>2</sup> in cross section, is suspended between two small metal clamps, C<sub>1</sub> and C<sub>2</sub>. The vertical position of the lower clamp C<sub>1</sub> is fixed by attachment to the base B fitting inside the inner Pyrex tube J<sub>1</sub> and suspended from the main column A of the apparatus by two small stainless-steel rods as shown. The upper clamp C<sub>2</sub> is attached to the lower end of a 1.0 mm nichrome rod, its upper end connecting with a strain gage G. The inner Pyrex tube is filled with sufficient water to surround sample and clamps. Pure nitrogen is bubbled very slowly through the water in order to suppress oxidation of the sample. The temperature of the sample and suspension system is controlled by circulation of water from a thermostat through the outer jacket J<sub>2</sub> as shown.

The strain gage is attached to a brass block which slides on the main column, its position being controlled as shown in Figure 1 by the screw S of low pitch. The screw is driven by a low-speed, reversible d.c. motor; the length may be varied at any constant rate from 0.02 to 0.5 cm min<sup>-1</sup>. The lower rate, corresponding to an extension of 0.1 to 0.2 per cent per min, was used in the experiments reported here. The strain gage (Statham Instrument Company, Transducer Model G-1) has a capacity of 120 g and a linear response of 0.16 mv per g under an applied e.m.f. of 9 v. The deflection of the strain gage is negligible, being only 0.02 mm at full load. The output of the strain gage is connected to a Honeywell recorder giving full scale deflection at 10 mv. A deflection of 1 mm corresponds to a load of ca. 0.2 g. The instrument was calibrated directly by addition of known weights before each run; in experiments of long duration calibration was repeated in the course of the run, the sample being temporarily cooled and the tension relaxed. Stress-strain curves were obtained by recording the force while the sample was elongated at the aforementioned rate. An electrical pulse at each turn of the screw (S in Figure 1) was recorded simultaneously with the output of the gage, thus permitting determination of the length from the record. Stress-strain curves for both crystalline (racked) and amorphous (shrunken) fibers were determined in this manner. Upon reversing the motor driving the screw S, the stress-strain curve was in each case found to deviate inappreciably from the curve established during elongation. Hysteresis is therefore negligible over the range of elongation examined (7% for racked samples, 150% for amorphous).

## RESULTS

*Dependence of length of racked samples on temperature and force.*—The relation of stress to strain was determined for limited extensions of the samples in the comparatively inextensible racked state for several temperatures from 0 to 30° but not exceeding the shrinkage temperatures (ca. 35°, see below). Results are shown in Figure 2 for sample f-1 at several temperatures. It will be observed that the length  $L^c$  for zero force, established by extrapolation, decreases by several per cent with rise in temperature. Simultaneously, the initial modulus decreases from  $1.7 \times 10^9$  dynes  $\text{cm}^{-2}$  at 0° to  $0.4 \times 10^9$  dynes  $\text{cm}^{-2}$  at 30°. The modulus of elasticity of native collagen in water at room temperature is approximately an order of magnitude greater, i.e., ca. 1 to  $3 \times 10^{10}$  dynes  $\text{cm}^{-2}$ . The difference may be indicative of a considerably higher percentage of crystal-

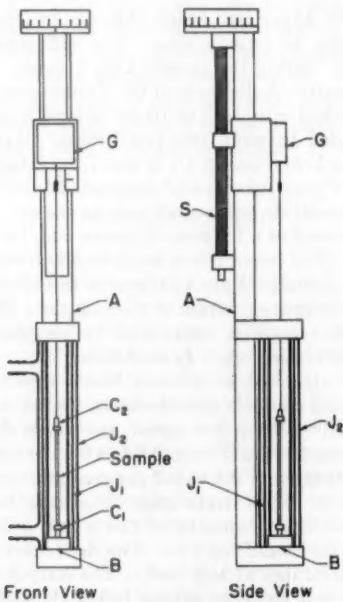


FIG. 1.—The dynamometer.

linity in collagen. Both changes are doubtless due to a slight decrease in the degree of crystallinity (i.e., partial melting) as the shrinkage temperature  $T_s$  (see below) is approached. Up to 30° the changes with temperature are essentially reversible.

Values of  $L^c$ , established as in Figure 2 for temperatures below 35°, are plotted against the temperature in the upper portion of Figure 3. Irreversible shrinkage occurs at 35° ( $T_s$ ) and above. The lower points represent lengths of the fully shrunken (amorphous) samples, those below 35° having been obtained by shrinking above 35° and then lowering the temperature.

*Shrinkage temperatures.*—Upon raising the temperature shrinkage occurs abruptly at a temperature easily defined within narrow limits under given condi-

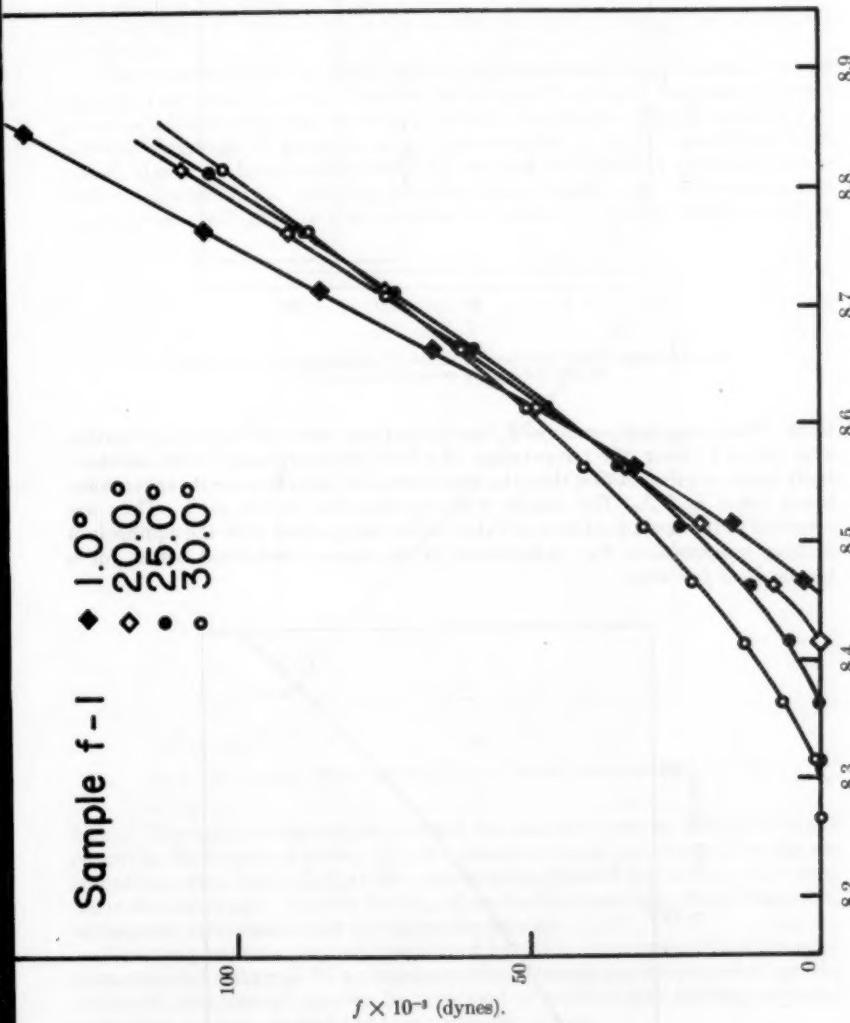


Fig. 2.—Force-length curves for racked sample f-1 prior to shrinkage.

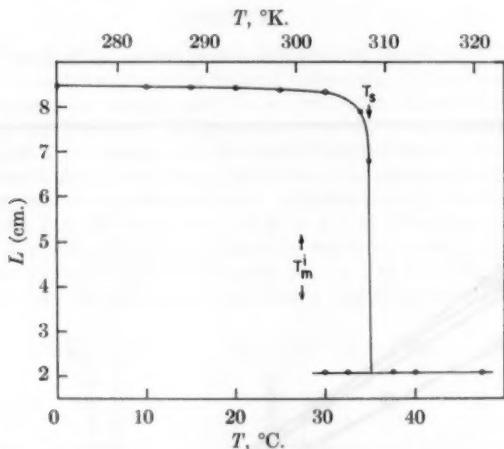


FIG. 3.—Length under zero force for sample f-1 plotted against temperature.  
Results obtained by extrapolation to  $f = 0$ .

tions. Shrinkage temperatures  $T_s^i$  under no force were determined by heating at a rate of  $2^\circ/\text{hour}$ , the temperature at which an amorphous "bulb" substantially larger in cross section than the semicrystalline sample made its appearance being taken as  $T_s^i$ . The results were reproducible within  $\pm 1^\circ$ . They are recorded in the second column of Table IV for comparison with the equilibrium melting temperatures  $T_m^i$ , determined in the manner described below, for a tensile force  $f$  of zero.

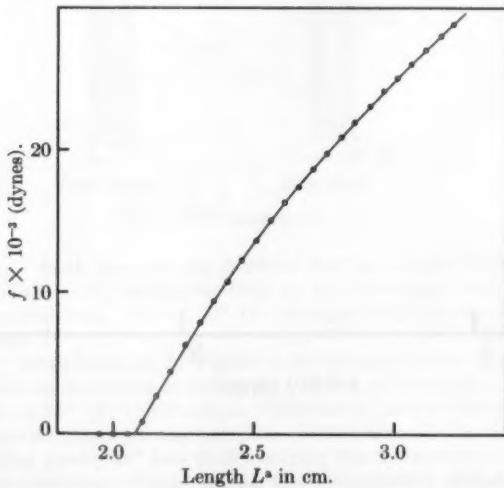


FIG. 4.—Force-length curve for sample f-1 in the amorphous state at  $35^\circ$ .

As is evident from Figure 3, sample f-1 shrinks to about one fourth of its initial length. Similar shrinkages are exhibited by the other samples according to results presented in Table III. The degree of shrinkage approximates that exhibited by tendon collagen. Noncrosslinked samples of racked rubber shrink by a much larger factor of about eleven<sup>4</sup>. The degree of shrinkage diminishes with the degree of crosslinking in the manner required by theory<sup>6</sup>, as was shown previously.

The transformation of these racked rubber samples upon heating bears a striking resemblance to the familiar shrinkage of collagen and other fibrous proteins including keratin, epidermin, myosin and fibrin. The phenomenon of thermal shrinkage of proteins, or supercontraction as it has sometimes been called, appears to be characteristic of the melting of crystalline polymers having high axial orientation. Melting and simultaneous shrinkage is sometimes followed (upon cooling) by recrystallization to the same or to a different crystalline

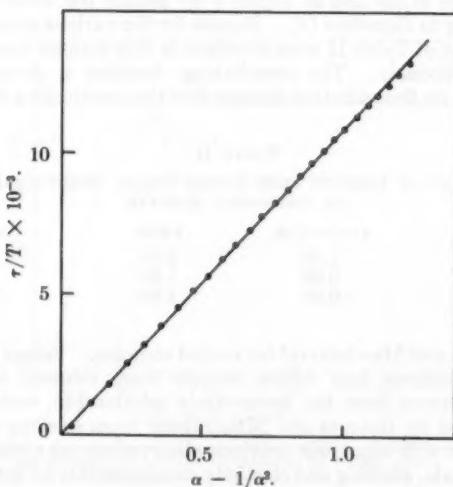


FIG. 5.—Stress-strain relation for sample f-1 at 35° plotted according to Equation (4).

form. The native  $\alpha$ -crystalline proteins, for example, may be converted to the  $\beta$ -form in the retracted state. There appears to be no justification for the assumption, often implied, that the subsequently formed crystalline state produces the shrinkage. Rather, melting of the initial anisotropic state is essential, subsequent recrystallization being only incidental.

Most important is the fact established by these experiments, that the phenomenon of shrinkage is by no means restricted to polypeptides or other specific polymeric structures. It may be presumed to occur in any suitably oriented crystalline polymer comprising long molecular chains.

*The stress-strain relation for amorphous samples.*—The curve relating force to length for sample f-1 at 35° is shown in Figure 4. Points obtained during retraction are virtually coincident with those for extension and therefore are not distinguished on the graph. In Figure 5 the stress  $\tau$  referred to the am-

phous cross section in the undeformed state is plotted according to the equation of state given by rubber elasticity theory<sup>6</sup>

$$\tau/T = (R\rho \langle \alpha \rangle_0^2 / M_0 \bar{v}) (\alpha - 1/\alpha^2) \quad (4)$$

where  $\rho$  is the effective fraction of isoprene units which are crosslinked,  $M_0$  is the molecular weight of an isoprene unit,  $\bar{v}$  is the specific volume,  $R$  is the gas constant,  $\alpha = L/L_i^0$  is the elongation ratio,  $L_i^0$  being the "isotropic" length for  $f = 0$  in the amorphous state at the temperature  $T$ , and  $\langle \alpha \rangle_0$  is the mean dilation factor<sup>2,6</sup>. The experimental points are well represented, over the limited range of extension of concern in the present investigation, by the straight line drawn in Figure 5. It has been unnecessary therefore to include in the equation of state the additional term in  $(1 - 1/\alpha^2)$  which ordinarily is required<sup>8-10</sup>.

From the slope of the line in Figure 5 we deduce the value of the product  $\rho \langle \alpha \rangle_0^2$  according to Equation (4). Results for the various samples recorded in the second column of Table II were obtained in this manner from the observed stress-strain relationship. The crosslinking densities  $\rho$  given in the third column are based on the radiation dosages and the crosslinking efficiency estab-

TABLE II  
SUMMARY OF RESULTS FROM STRESS-STRAIN MEASUREMENTS  
ON AMORPHOUS SAMPLES

Sample	$\rho \langle \alpha \rangle_0^2 \times 10^3$	$\rho \times 10^3$	$\langle \alpha \rangle_0$
b-2	1.30	2.17	0.78
f-1	0.98	1.56	.79
l-1	0.62	1.04	.77

lished by Roberts and Mandelkern<sup>3</sup> for racked samples. Values for the dilation factor given in column four follow directly from columns two and three. These values, deduced from the stress-strain relationship, compare favorably with those derived by Roberts and Mandelkern<sup>3</sup> from swelling measurements. Thus, in common with numerous previous observations on systems crosslinked in the isotropic state, swelling and elasticity measurements on networks imposed on the racked state yield concordant results.

*Equilibrium between racked and amorphous states.*—Just as in the case of collagen<sup>1</sup>, it is essential to recognize the nonidentity of the shrinkage temperature  $T_s$  with the "melting" temperature  $T_m$  at which equilibrium prevails between coexisting racked (semicrystalline) and amorphous phases, or regions, at given pressure  $P$  and tensile force  $f$ . When  $f = 0$ , we employ the symbols  $T_{s,i}$  and  $T_{m,i}$  signifying an isotropic amorphous phase. Also, a subscript " $m$ " is applied to the equilibrium temperature  $T$  occurring in Equations (1)-(3) in consideration of the fact that  $T$ , or  $T_m$ , is to be regarded as a melting point under the tensile force  $f_{eq}$ . If the sample is maintained at  $T \geq T_s$ , a shrunken zone(s) appears and, if the force is maintained constant, it spreads throughout the length of the fiber. In order to arrest the transformation once it is initiated, the force must be increased substantially or the temperature lowered. In order to achieve stable coexistence of crystalline and amorphous regions, the temperature must be lowered 5 to 10° below  $T_s$ , the force remaining constant. The equilibrium melting temperature  $T_m$  is therefore substantially lower than

$T_s$ , and the difference between them represents the superheating required for the formation of a macroscopic amorphous region.

In the experiments to be described, the following procedure was adopted. After mounting the sample in the dynamometer, the clamps are fixed at a distance apart somewhat less than the initial sample length  $L^e$ . The temperature is then raised to an arbitrarily chosen temperature  $T$  a few degrees above the shrinkage temperature  $T_s$  for  $f = 0$ , and thereafter the temperature is maintained constant. Melting proceeds in one or more sections of the sample with the development of amorphous zones across the sample section. Inasmuch as the total length is fixed, the sample exerts a retractive force which increases as melting progresses. The force approaches a constant value after ca. 15 minutes. If the length is now increased slightly, the concomitant increase in force initially developed is observed to decay toward the former value; the initial decrease in force brought about by a small decrease in length is followed similarly by an increase in force. An example is shown in Figure 6.

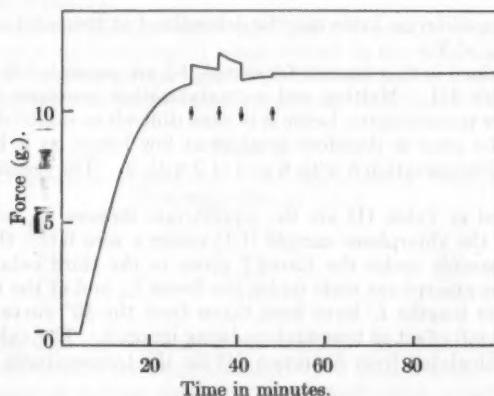


FIG. 6.—Illustrative plot of determination of equilibrium force. Points at which the length was increased or decreased are indicated by vertical arrows.

Evidently, recrystallization or melting at the interface(s) between semicrystalline (racked) and amorphous zone(s) occurs to the extent required for re-establishment of phase equilibrium. A too-drastic increase in length cannot, however, be accommodated with restoration of the initial equilibrium force.

In accordance with the observations cited, the equilibrium force  $f_{eq}$  at a given temperature may be bracketed within reasonably narrow limits by manipulating the length of the partially shrunken sample until the force remains constant with time for at least 1 hour. The equilibrium force is independent of the sample length, provided merely that semicrystalline and amorphous regions coexist, i.e., the equilibrium force is independent of the amount of each phase.

Having established  $f_{eq}$  at one temperature, additional points ( $T_m, f_{eq}$ ) may be determined on the same sample merely by resetting the temperature and, preferably, with simultaneous reduction of the length in order to allow advancement of the amorphous zone(s) to yield fresh interfaces. Once interfacial regions have been established through partial transformation of the sample at

TABLE III

## PHASE EQUILIBRIUM DATA FOR SAMPLE f-1

(Dimensions in the isotropic amorphous state: cross section  
 $= 76.3 (\pm 0.5) \times 10^{-4} \text{ cm}^2$ ;  $L_i^a = 2.078 \text{ cm}$ )

$T_m$ (°K)	Order in se- quence of detn.	$f_{eq}$ $\times 10^{-2}$ , dynes	$\tau_{eq}$ $\times 10^{-4}$ , dynes cm $^{-1}$	$L^c$ , cm	$L^a$ , cm	$-\Delta L$	$J(1/T_m)$ $\times 10^4$
303.2	7	2.7	3.5	8.335	2.145	6.190	9.2
305.7	6	5.0	6.6	8.350	2.215	6.135	18.4
	8	6.5	8.5	8.365	2.255	6.110	
308.2	5	9.0	11.8	8.390	2.335	6.055	27.3
310.7	4	13.5	17.7	8.415	2.495	5.920	36.5
313.2	3	17.5	22.9	8.445	2.665	5.780	45.5
	9	17.8	23.4	8.445	2.675	5.770	
315.7	2	24.0	31.5	8.485	2.955	5.530	55.2
318.2	1	28.9	37.8	8.510	3.195	5.315	64.6

$T_m > T_i^i$ , the equilibrium force may be determined at temperatures  $T_m$  in the range  $T_m^i < T_m < T_i^i$ .

Results obtained in this manner for sample f-1 are presented in columns one to three of Table III. Melting and recrystallization processes become very slow at the lower temperatures, hence it is more difficult to establish the equilibrium force. The error is therefore greatest at low forces, as is borne out by comparison of determination 8 with 6 and of 9 with 3. The results are plotted in Figure 7.

Also included in Table III are the equilibrium stresses  $\tau_{eq}$  referred to the cross section of the amorphous sample (f-1) under a zero force, the lengths  $L^c$  of the racked sample under the forces  $f$  given in the third column, and the lengths  $L^a$  in the amorphous state under the forces  $f_{eq}$  and at the temperatures  $T_m$ . The former lengths  $L^c$  have been taken from the 30° curve in Figure 2, the relatively small effect of temperature being ignored. The values given for  $L^a$  have been calculated from Equation (4) for the temperatures  $T = T_m$  and

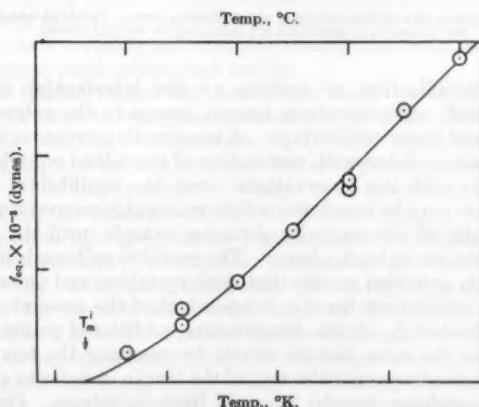


FIG. 7.—Force for phase equilibrium for sample f-1 plotted against the absolute temperature.

stresses  $\tau_{eq}$ . The differences  $-\Delta L = L^a - L^e$  are recorded in the next to the last column of Table III.

The isotropic melting point  $T_m^i$  of sample f-1, obtained by extrapolation to  $f_{eq} = 0$  in Figure 7, is 302° K. Results for the various samples are given in Table IV. Owing to the previously mentioned difficulty of establishing equilibrium at low forces, the values of  $T_m^i$  are subject to an error of ca.  $\pm 2^\circ$ . An increase in the melting point with degree of crosslinking is suggested by the results. Whereas crosslinking in the isotropic state is known to lower the melting point<sup>11</sup>, theoretical considerations<sup>6</sup> suggest that the melting point should be increased by crosslinking in the highly ordered state. Roberts and Mandelkern in the preceding paper<sup>8</sup> report consistently higher melting points for samples crosslinked in the racked state. Although their melting temperatures, obtained by comparatively rapid heating of recrystallized samples, are admittedly some 20° below the equilibrium values, they have pointed out that, according to their Figure 3, our sample l-1 should melt 7° higher than b-2 under the conditions employed by them. The difference is identical with that found by us and reported in our Table IV.

*Recrystallization.*—Samples removed from the dynamometer after complete melting were nonbirefringent when viewed in the polarizing microscope. However, after standing several days at 20–25°, specimens of each sample were observed to develop substantial birefringence, the direction of higher refractive

TABLE IV  
COMPARISON OF SHRINKAGE AND EQUILIBRIUM MELTING  
TEMPERATURES AT  $f = 0$

Sample	$T_s^i$ , ° K	$T_m^i$ , ° K
b-2	310	299
f-1	308	302
l-1	311	306

index coinciding with the long axis of the sample. The birefringence vanished upon heating above 30°; the exact temperature of disappearance was not ascertained. Samples of rubber similarly crosslinked (with  $\gamma$ -radiation) in the amorphous state without stretching offered no evidence of either birefringence or depolarization, even after standing many days at 20 to 25°. We interpret the spontaneous generation of birefringence in the former samples as clear evidence of recrystallization with preferred orientation along the initial axis of elongation. Depolarization rather than birefringence should have been observed if the latter samples had crystallized; spontaneous development of birefringence could not have been expected from their molecularly isotropic structures. The absence of depolarization indicates absence of crystallinity.

The observations cited require that the melting point of the racked, cross-linked samples must exceed 25°, and hence offer partial confirmation for the values deduced from the stress studies. They also indicate a latent "memory" in the network structures, to the extent that recrystallization restores the original preferred axis. Finally, it is noteworthy that recrystallization in these samples requires a remarkably small degree of supercooling<sup>12</sup>.

#### DISCUSSION

By introducing the stress  $\tau_{eq}$  (referred to the amorphous isotropic cross section  $A_i = V/L_i^a$ ) in Equations (1) and (3) and by integrating them in the

approximation that  $\Delta S$  and  $\Delta H$  are constant with temperature, we obtain

$$\tau_{eq} = -(\Delta S/V)L_i^a \int_{T_m}^{T_m} (\Delta L)^{-1}dT = (\Delta S/V)L_i^a I(T_m) \quad (5)$$

and

$$\tau_{eq}/T_m = (\Delta H/V)L_i^a \int_{1/T_m}^{1/T_m} (\Delta L)^{-1}d(1/T) = (\Delta H/V)L_i^a J(1/T_m) \quad (6)$$

where  $\Delta S/V$  and  $\Delta H/V$  represent the entropy and enthalpy changes upon melting of 1 cc of the fiber ( $V$  being the volume of the sample in the amorphous state). The functions  $I(T_m)$  and  $J(1/T_m)$  defined by these equations may be evaluated by graphical integration employing results such as are given in Table III. The latent entropy and enthalpy changes associated with transformation of the sample from the racked (semicrystalline) to the amorphous state may then be computed in accordance with Equations (5) and (6). Under

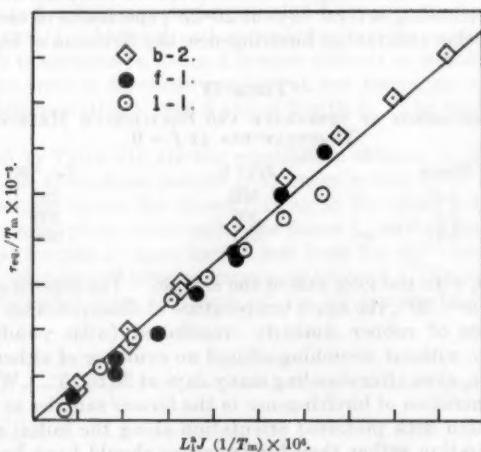


Fig. 8.—Plots of equilibrium stresses according to Equation (6).

the assumption of constancy of  $\Delta H$  and  $\Delta S$  with temperature over the small range concerned,  $\Delta H = T_m^4 \Delta S$ ; hence, evaluation of either  $I(T_m)$  or  $J(1/T_m)$  should suffice for the task at hand. The latter procedure, leading directly to  $\Delta H$ , is presented herein; equivalent results may be deduced by the former procedure involving graphical integration according to Equation (5).

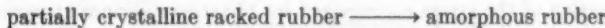
Values of  $L_i^a J(1/T_m)$  for sample f-1, established by graphical integration of  $(\Delta L)^{-1}$  plotted against  $1/T$ , are given in the last column of Table III. These results, together with those similarly obtained for the other two samples, are shown in Figure 8 where  $\tau_{eq}/T_m$  is plotted against  $L_i^a J(1/T_m)$ . The results for the three samples, differing in degrees of crosslinking (but not in degree of crystallinity), are in close accord. The slope of the straight line drawn

through the three sets of points determines  $\Delta H/V$  according to Equation (6). We thus obtain

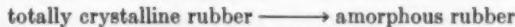
$$\Delta H/V = 4.10 \text{ cal cc}^{-1}$$

where  $V$  is the volume of the sample in the amorphous state.

The quantity  $\tau_{eq}$  denotes the tensile stress required for equilibrium at  $T_m$  between the adjoining (but macroscopically distinct) zones, which may be regarded as separate phases. The latent changes  $\Delta H$  and  $\Delta S$  computed above represent differences between the enthalpies and entropies for the two zones, or phases; that is, they refer to the process



The latent changes may be ascribed entirely to the melting of that fraction which is crystalline without commission of appreciable error. To be sure, molecular chains in the intervening amorphous matrix are probably in a state of strain, but in the very good approximation that amorphous rubber exhibits ideal rubber elasticity<sup>12</sup> (i.e., that  $(\partial H/\partial L)_{V,T} = 0$ ), the associated enthalpy change is zero. Hence, we may obtain the latent enthalpy change for the hypothetical process



merely by dividing  $\Delta H/V$  given above by the fractional degree of crystallinity, which according to data given in Table I is about 0.24 ( $\pm 0.02$ ). Thus, with further introduction of the specific volume,  $1.10 \text{ cc g}^{-1}$

$$\Delta H_{(c \rightarrow a)} = 18.7 \pm 2 \text{ cal g}^{-1}$$

The major source of error in this value arises from the uncertainty in the degree of crystallinity, which, in turn, stems from the inaccuracy in the x-ray crystal density.

Under the assumption that  $T_m^i$  represents the melting temperature of crystalline rubber when subject to no elastic deformation, the latent entropy for the latter hypothetical process may be obtained merely by dividing  $\Delta H_{(c \rightarrow a)}$  by  $T_m^i$ . We thus find

$$T_m^i = 302^\circ \text{ K}$$

$$\Delta H_u = 1280 \pm 150 \text{ cal per mole of C}_5\text{H}_8$$

$$\Delta S_u = 4.2 \pm 0.4 \text{ cal deg}^{-1} \text{ per mole C}_5\text{H}_8$$

These results compare favorably with those previously obtained by Roberts and Mandelkern<sup>13</sup> from the depression of the melting point of vulcanized rubber by diluents, namely

$$T_m^i = 301^\circ \text{ K}$$

$$\Delta H_u = 1040 \pm 60 \text{ cal mole}^{-1}$$

$$\Delta S_u = 3.5 \pm 0.2 \text{ cal deg}^{-1} \text{ mole}^{-1}$$

We conclude that the transformation of highly orientated racked rubber, crosslinked by  $\gamma$ -radiation, to the amorphous state can be satisfactorily treated

as a phase change. In particular, the dependence of the equilibrium stress on the temperature is in complete accord with the requirement of thermodynamic equilibrium between phases.

### SUMMARY

Highly oriented natural rubber samples of Roberts and Mandelkern, prepared by racking and subsequently crosslinked using  $\gamma$ -radiation, undergo a spontaneous shrinkage upon melting which closely resembles the shrinkage of collagen. If the transformation is arrested by application of a tensile force, a state of equilibrium may be established between two distinct zones, or phases, one being totally amorphous (shrunken) and the other unchanged (i.e., racked). Determination of the stress  $\tau_{eq}$  required for phase equilibrium at various temperatures is described. Extrapolation to  $\tau_{eq} = 0$  gives equilibrium melting temperatures  $T_m^i$ , which are about 8° below the temperatures  $T_s^i$  for spontaneous shrinkage. The heat of transformation of racked to amorphous rubber calculated from the dependence of  $\tau_{eq}$  on  $T$  is 4.5 cal g<sup>-1</sup>. Since the degree of crystallinity is only 0.24, the heat of fusion calculated for 1 g of crystalline rubber is ca. 19 cal, which agrees satisfactorily with the value 15.3 cal, deduced by Roberts and Mandelkern through use of the melting point depression method. The shrinkage of racked rubber displays all of the important features associated with the similar contraction of fibrous proteins.

### ACKNOWLEDGMENTS

The authors are indebted to Drs. Mandelkern and Roberts for providing the samples used in this investigation and to Dr. Mandelkern for detailed suggestions and criticisms with reference to the interpretation of the results and the preparation of the manuscript.

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## MELTING AND GLASS TRANSITIONS IN POLYISOBUTYLENE \*

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### INTRODUCTION

The purpose of this work was to investigate the crystallization behavior of uncompounded, unstressed polyisobutylene and butyl rubber. Glass transition data obtained during the work are also reported. The data were determined dilatometrically. The work was prompted by a literature survey<sup>1</sup> which collected transition data on elastomers. It was found that crystallization information for polyisobutylene and butyl rubber was based largely on x-ray studies of these polymers under high elongation. In fact, it has been assumed generally that these polymers would crystallize only when highly oriented, as by stretching. Because of the resistance of polyisobutylene to ordering when in the unstressed state, no measurements of optimum crystallization temperature or melting temperature,  $T_m$ , have previously been reported. Information of this type is important because of its bearing on the mechanical behavior of a polymer.

Many types of elastomers will crystallize readily if oriented by a large stress. However, only those having relatively simple structures crystallize readily under zero stress. Such behavior is, of course, a limiting factor in low-temperature serviceability. Polyisobutylene might seem at first to have the required simplicity of structure; however, steric hindrance of the side methyl group forces the chain to crystallize in a helical configuration having a molecular repeat distance of 18.6 Å, as shown by Fuller, Frosch, and Pape<sup>2</sup>. This is the greatest repeat distance of any of the elastomers, suggesting that a lengthy exposure period would be required if ordering were to occur at all. A clue to ordering in an isobutylene copolymer was furnished by Gehman, Woodford, and Wilkinson<sup>3</sup>, who reported that a butyl tread stock showed a greatly increased torsional stiffness after storage for about 40 days at -30° C. The aged butyl sample exhibited an x-ray diffraction pattern suggestive of crystallization. These results may be the first showing crystallization in a butyl polymer essentially free of stress. In other work, Radi and Britt<sup>4</sup>, using equilibrium temperature-retraction techniques with samples elongated 300 per cent initially, found that two types of butyl polymers showed optimum crystallization rates at -30° and -41° C. The aggregate of these results suggests that crystallization might occur in unstressed polyisobutylene if sufficient time were allowed, and indicates an optimum rate in the range of -30° to -40° C. This is reasonable by comparison with natural rubber, which has a glass transition temperature very close to that of butyl rubber, and an optimum crystallization rate at about -25° C.

\* An original publication. Presented before the Rubber Division of the American Chemical Society, Cincinnati, Ohio, May 14-16, 1958.

## EXPERIMENTAL

Dilatometric techniques described by Bekkedahl<sup>6</sup> were followed in this work. The capillary tubing of the dilatometers of about 2 mm inside diameter was of the precision-bore type supplied by the Fischer and Porter Company, Hatsboro, Pennsylvania. During calibration, the bore volume of this tubing was found to be constant within  $\pm 0.0001$  ml/mm over its entire length. This degree of precision falls within experimental error and makes it unnecessary to correct the volume of the confining fluid for variations in the bore.

Each raw polymer sample was first pressed into a  $6 \times 6 \times 0.075$ -inch sheet for 15 minutes at  $120^\circ$  to  $135^\circ$  C. This procedure removed nearly all of the air and rendered the sample transparent so that any remaining air bubbles could easily be excluded. It was necessary to handle the samples as small pieces, because the polymers were so tacky that large strips or chunks could not be pushed into the dilatometer bulb without entrapping large amounts of air. Therefore, the deaerated samples were cut into small cubes and about 5 to 7 grams were charged into the dilatometer with tweezers. Silicone Oil Type SF (81)-40 (General Electric Company) was used as the confining fluid. This oil has previously been shown to be suitable for such a purpose<sup>6</sup>. It has a low vapor pressure, low surface tension, and no swelling effect on the polymers as determined by a three-month swell test at room temperature. It was determined experimentally that the linear expansivity coefficient of this oil is constant from  $25^\circ$  to  $-100^\circ$  C. Each dilatometer was cleared of air under vacuum, and was considered to be properly evacuated if the oil meniscus changed no more than 1 mm between atmospheric pressure and full vacuum. Meniscus and reference heights for the dilatometer were measured with a cathetometer to  $\pm 0.01$  cm.

Long-term exposures at low temperature were carried out in a cold bar patterned after a device originally described by Mooney and Wolstenholme<sup>7</sup>. This consists of 16 separate cold baths operating between  $0^\circ$  and  $-60^\circ$  C, controlled by the temperature gradient between a water bath at  $0^\circ$  C and a dry-ice bath at  $-72^\circ$  C. With this cold bar, temperatures were maintained within  $\pm 1$  degree for months at a time. Temperatures were measured to  $\pm 0.1^\circ$  C by means of thermocouples.

Variations in the height of the meniscus were converted to density changes for each sample. The data were corrected for the emergent stem and for volume changes in the silicone oil and Pyrex bulb. The emergent stem correction becomes quite significant with silicone oil or other organic fluids that are used in low-temperature dilatometry, because their expansivity is often greater than that of the sample. It was shown during this work that the usual assumption that the temperature inside the entire emergent stem approaches the surrounding air temperature is not strictly correct. Measurements made inside the capillary by means of fine thermocouple wires showed that there was a temperature gradient extending as much as 12 cm above the bath liquid level, even though the entire emergent stem was exposed to ambient temperatures. Taking this gradient into account, a corrected emergent stem formula was obtained as follows:

$$\text{Emergent-stem correction} = 0.94 K N (T_B - T_A),$$

where

$K$  is the difference between expansivity coefficients of the confining fluid and Pyrex glass

$N$  is the height of the meniscus above bath level

$T_B$  is bath temperature

$T_A$  is air temperature

The quantity 0.94 was found to be applicable as an average factor at all bath temperatures, to correct for the temperature gradient in the lower part of the capillary tubing.

### RESULTS

Expansivity curves were determined for Vistanex L-100 and L-140 and for uncompoounded butyl rubbers including Enjay Butyls 035, 150, 215, 217, 218, and 325. For these measurements, the samples were cooled from 25° to -95°C at the rate of 0.5 degree per minute. The temperature was maintained constant at each 5-degree interval for 10 minutes before taking a reading. As expected, no evidence of crystallization in any of the polymers was found in these initial rapid cooling tests. However, glass-transition temperatures were observed, and since it is believed that these have not all been published before, they are reported here in Table I.

TABLE I  
GLASS-TRANSITION TEMPERATURES OF POLYISOBUTYLENES  
AND BUTYL RUBBERS

Polymer	Unsaturation, mole per cent	$T_g$ , °C
Butyl 325	2.1-2.5	-70
Butyl 215	1.5-2.0	-71
Butyl 217	1.5-2.0	-71
Butyl 218	1.5-2.0	-71
Butyl 150	1.0-1.4	-72
Butyl 035	0.6-1.0	-73
Vistanex L-100	0	-76
Vistanex L-140	0	-76

The difference in slope of the cooling curve above and below  $T_g$  is very small and a certain amount of subjectivity is involved in determining the breaking point. However, it is felt that these values of  $T_g$  are accurate to within  $\pm 1$  degree.

As can be seen in Table I, the  $T_g$  values of these polymers are in the same range as those of *cis*-1,4-polyisoprene (natural rubber). It is not certain why relatively small amounts of isoprene can increase  $T_g$  of the copolymer as much as 6 degrees. It might be concluded that isoprene enters the copolymer in the 1,2 configuration since 1,2-polyisoprene could be expected to have a relatively high  $T_g$ . However, ozonolysis studies<sup>8</sup> indicate only 1,4 polymerization of the isoprene in butyl rubber. The change in  $T_g$  may imply then that isoprene assumes the trans 1,4 configuration in the copolymer, since in this form, in the homopolymer, its  $T_g$  also is higher than in natural rubber. However, the difference in  $T_g$  between *trans*-1,4-isoprene and polyisobutylene is probably not enough to account for the large effect of the small isoprene content of the butyl rubbers. The  $T_g$  results were taken from only one set of samples, but the trend of  $T_g$  with the degree of unsaturation seems real. The application of data of this kind to aid in the analysis of the structure of a copolymer provides interesting speculation.

The first observation of crystallization in polyisobutylene was made on samples in the cold bar, as shown in Figure 1. Vistanex L-100 and L-140 began

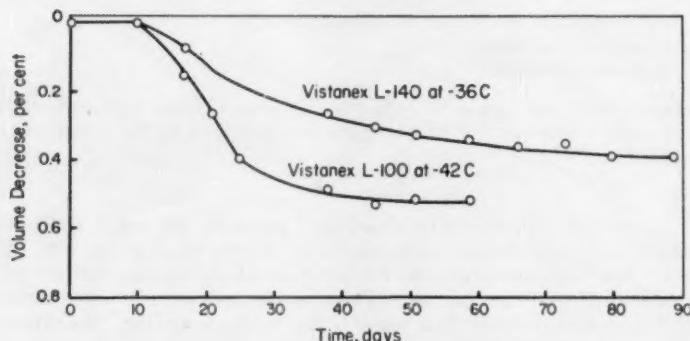


FIG. 1.—Crystallization of polyisobutylene.

to show a characteristic volume decrease after about 10 days at  $-42^{\circ}$  and  $-36^{\circ}$ , respectively. An approximate degree of crystallinity for Vistanex L-100 after equilibration at  $-42^{\circ}\text{ C}$  was calculated from the density of the amorphous polymer ( $0.918\text{ g/cm}^3$ ), the density of the partially crystallized material extrapolated to  $20^{\circ}\text{ C}$  ( $0.926$ ), and the density of the unit crystal, which, according to Bunn<sup>9</sup>, is  $0.96$ . These data indicate that the polymer was about 20 to 25 per cent crystalline, which is reasonable by comparison with results for other elastomers.

Measurements of the rate of crystallization of Vistanex L-100 at various temperatures are shown in Figure 2. The sample exposed at  $-55^{\circ}$  did not crystallize in 18 months. This left only three curves from which the rate could be determined. However, the rate data are known to follow what appears to be a normal distribution curve, as shown first by Wood<sup>10</sup> for natural rubber. The half-time for crystallization plotted against temperature, as in Figure 3,

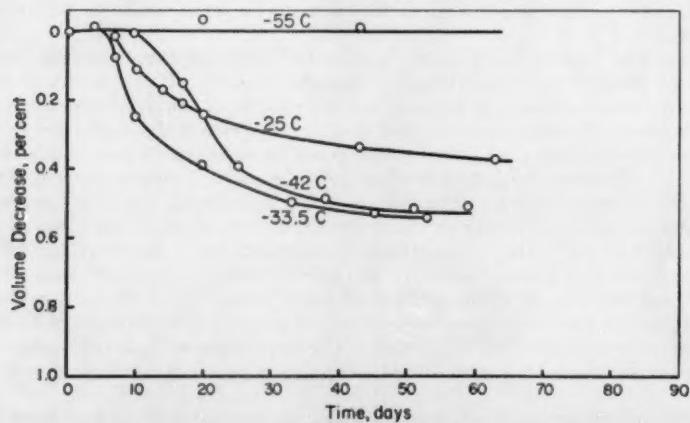


FIG. 2.—Volume-time relations during crystallization of polyisobutylene.

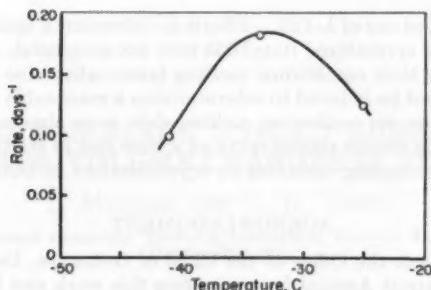


FIG. 3.—The crystallization rate of polyisobutylene as a function of temperature.

indicates that the maximum rate of crystal formation occurs near  $-33^{\circ}\text{ C}$ . It is assumed that essentially the same optimum temperature would be found for butyl rubber, since the small percentage of unsaturation in butyl should not significantly change the effect of temperature on crystallization rate, even though it can retard materially the rate of crystal growth.

The effect of copolymerization in polyisobutylene on the rate of crystal growth can be seen by examining the results of attempts to crystallize butyl rubbers. Over a period of a year and a half, at temperatures of  $-20^{\circ}$  to  $-40^{\circ}$ , only one sample crystallized. This sample was Butyl 035, which contains the least unsaturation of all the butyl polymers. In this material (exposed at an average temperature of  $-25^{\circ}$ ), evidences of crystallinity first began to appear after about 6 months, and the decrease in specific volume then continued to an apparent maximum after an additional 6 months. In view of the lengthy test period required, it is not surprising that previous efforts to detect crystallization in unstressed butyl rubbers have not been successful.

Melting-point determinations for crystallized samples of Vistanex L-100 and L-140 were made following the slow melting technique prescribed by Evans, Mighton, and Flory<sup>11</sup>. Melting was carried out at an average heating rate of 1 degree per day, and over the last 5 degrees at 0.5 degree or less per day. The temperature was increased only when it appeared that the equilibrium volume had been attained at each temperature. Results for Vistanex L-100 are shown in Figure 4. A melting temperature of  $1.5 \pm 0.5$  degrees was indicated by three

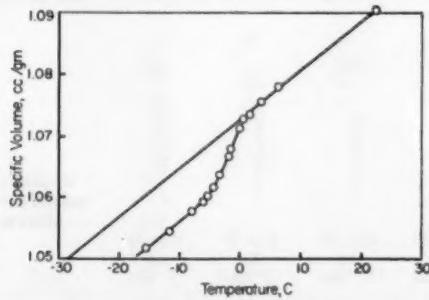


FIG. 4.—Melting curve of polyisobutylene.

samples of L-100 and one of L-140. Efforts to determine a melting temperature using the sample of crystallized Butyl 035 were not successful. The crystallites were melted below their equilibrium melting temperature due to an equipment failure and could not be induced to reform within a reasonable period at a lower temperature. Thus, no confirming melting data were obtained for butyl rubber. However, the results should serve as a base line in studying the effect of stress and of compounding variables on crystallization in butyl polymers.

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# CARBON-BLACK LOADED RUBBER VULCANIZATES: VOLUME CHANGES IN STRETCHING\*

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## INTRODUCTION

Previous measurements<sup>1</sup> of the volume changes accompanying the extension of vulcanized natural rubber have shown that, with compounds completely free of mineral fillers and undissolved particles, there is a small increase in volume at low extensions. This small expansion results from the hydrostatic component of the stretching force and can be readily calculated from the compressibility of the rubber. At higher extensions, there is a decrease in volume, and this has been related to the occurrence of crystallization<sup>2,4</sup>. In vulcanizates containing mineral fillers or solid particles relatively large increases in volume, attributed to vacuole formation around filler particles, may also accompany extension, but increases in volume due to this cause are small in vulcanizates containing reinforcing carbon black<sup>1,3</sup>. This paper describes an investigation into the crystallization in such vulcanizates by measurements of volume changes accompanying extension. The results are discussed in the light of a simple model recently developed to describe the stress-strain behavior of reinforced vulcanizates<sup>5</sup>.

## EXPERIMENTAL

Measurements were made on the following three types of vulcanizate:

- (1) Tire tread type vulcanizate (Mixes A & B).
- (2) Accelerated sulfur gum vulcanizate (Mix C).
- (3) Peroxide gum vulcanizate (Mixes D & E).

The compounding and vulcanizing details are given in the table.

Mix	A	B	C	D	E
Smoked sheet	100	—	100	100	—
GR-S	—	100	—	—	100
MPC black	50	50	—	—	—
Stearic acid	3	3	3	—	—
Zinc oxide	5	5	5	—	—
Sulfur	3	3	3	—	—
Mercaptobenzothiazole	1	1	1	—	—
Phenyl-2-naphthylamine	1	1	1	—	—
Di- <i>tert</i> -butyl peroxide	—	—	—	1½	1½
Vulcanization	45 min at 140° C	60 min at 150° C	45 min at 140° C	30 min at 155° C	30 min at 155° C

\* Reprinted from *Transactions of the Institution of the Rubber Industry*, Vol. 33, No. 1, pages 2-10 (1957).

Ring specimens were cut from a single flat sheet of each material with a rotary cutter; the rings had an outer diameter of 2 cm, an inner diameter of 1.4 cm, and were approximately 3 mm thick.

Volume changes were measured by hydrostatic weighing following the method adopted by Gee, Stern, and Treloar<sup>1</sup>. At low extensions eight rings were stretched at a time: this enabled changes in volume of one part in 30,000 to be determined. At high extensions only two rings were used, to avoid buckling the stretching frame, but the volume changes to be measured were much greater. It was necessary to use a more robust frame than that which was used by Gee, Stern and Treloar due to the much greater forces encountered in working with carbon loaded vulcanizates. The frame and the device for extending the samples are shown diagrammatically in Figure 1.

The weighings were carried out at 25° C in distilled water to which a little detergent had been added to facilitate wetting. The rings and frame were weighed under water, first in the unstretched position, and then with the rings at a chosen extension, and finally with the rings once more relaxed. This was repeated at least six times, and the change in volume then calculated from the mean of the difference in weight between the stretched and the unstretched

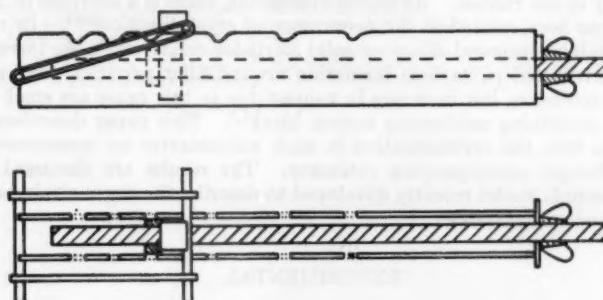


FIG. 1.—Sketch of extension apparatus.

states. At low extensions measurements were made 10 minutes after stretching, this being sufficient for thermal equilibrium to be reached. At high extension, where crystallization occurred, the weight was measured 20 minutes after stretching when the rate of change in volume due to crystallization had become negligible.

The distilled water was contained in a copper vessel with a Perspex front, which itself was within a large glass tank of water whose temperature was controlled by means of a toluene regulator and a 250 watt heater to  $\pm 0.01^\circ$  C. The temperature inside the copper vessel was read at each weighing with a Beckmann thermometer and did not vary more than  $\pm 0.02^\circ$  C in the course of a set of measurements. Exploratory measurements showed that temperature variations of this magnitude were sufficiently small to allow experiments to be made with the required accuracy.

Initial measurements showed that for the first 24 hours there was a continuous change in weight with time due to slight absorption of water by the rubber, and subsequently samples were immersed in water for three days before measurements were commenced and were kept immersed until all measurements were completed.

## EXPERIMENTAL RESULTS

Measurements of the fractional change in volume  $\Delta V/V$  obtained on the natural rubber-MPC black vulcanize (Mix A) are shown in Figure 2. The family of curves gives the change in volume with extension obtained on samples without previous extension and after previous extension to 50, 100, 200, 300 and 400 per cent. A similar series of measurements obtained on the GR-S-MPC black vulcanize (Mix B) is shown in Figure 3, except that with this vulcanize measurements were not obtained after 400 per cent previous extension as samples broke at this extension.

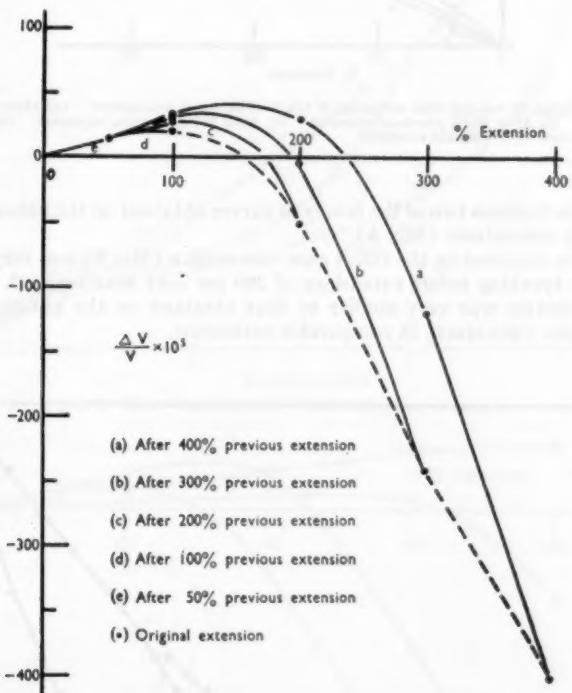


FIG. 2.—Change in volume with extension of natural rubber-MPC black vulcanize.

Figures 4 and 5 give families of stress-strain curves obtained on each of these vulcanizates without previous extension and after the chosen extensions of 50, 100, 200, 300 and 400 per cent.

Measurements on the natural rubber gum vulcanizes (Mixes C and D) are given in Figure 6. With the peroxide gum vulcanize (Mix D) the effect of previous extension on the volume change was negligible; in the case of the sulfur gum vulcanize (Mix C) the volume change increased slightly with previous extension but the differences in  $\Delta V/V$  were less than 10 per cent and are not sufficient to show conveniently in the figure. To facilitate comparison

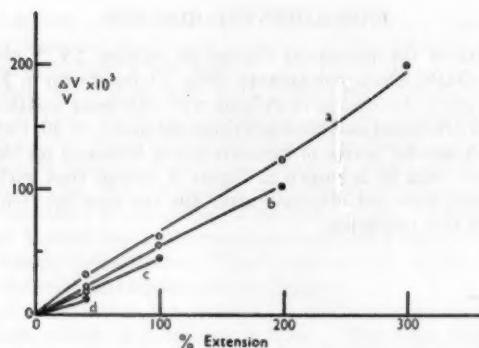


FIG. 3.—Change in volume with extension of GR-S-MPC black vulcanizate. (a) After 300% previous extension. (b) After 200% previous extension. (c) After 100% previous extension. (d) After 50% previous extension. (\*) Original extension.

Figure 6 also includes two of the family of curves obtained on the natural rubber MPC black vulcanizate (Mix A).

The data obtained on the GR-S gum vulcanizate (Mix E) was very limited, the sample breaking before extensions of 200 per cent were reached. The increase in volume was very similar to that obtained on the natural rubber-peroxide gum vulcanizate at comparable extensions.

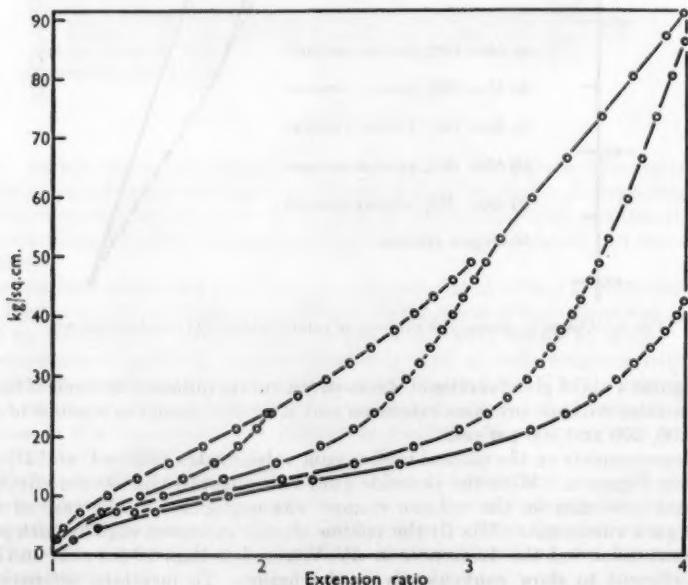


FIG. 4.—Stress-strain curves of natural rubber—MPC black vulcanizate.

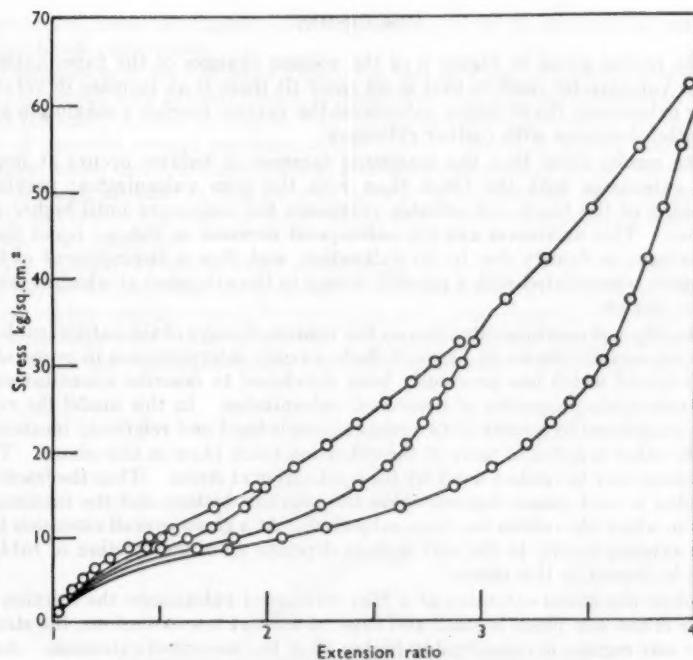


FIG. 5.—Stress-strain curves of GR-S-MPC black vulcanizate.

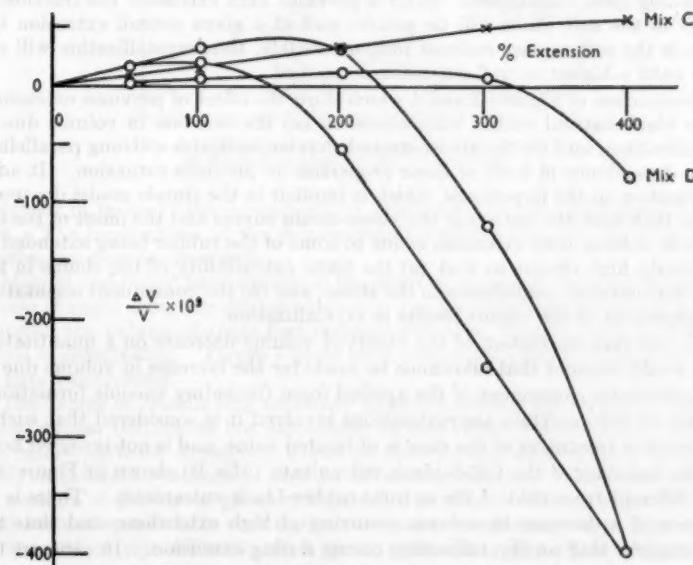


FIG. 6.—Change in volume with extension of natural rubber vulcanizates.

## DISCUSSION

The results given in Figure 6 of the volume changes of the three natural rubber vulcanizates confirm that in all cases (i) there is an increase in volume at low extensions, (ii) at higher extensions the volume reaches a maximum and thereafter decreases with further extension.

The results show that the maximum increase in volume occurs at much lower extensions with the black than with the gum vulcanizates; previous stretching of the black vulcanizates postpones the maximum until higher extensions. This maximum and the subsequent decrease in volume result from the increase in density due to crystallization, and thus a displacement of the maximum is associated with a parallel change in the extension at which crystallization begins.

The effect of previous extension on the volume changes of the natural rubber-black vulcanizate shown in Figure 2 finds a ready interpretation in terms of a simple model which has previously been developed to describe quantitatively the stress-strain properties of reinforced vulcanizates. In this model the rubber is considered to consist of two phases; one is hard and relatively inextensible, the other is soft and more of the extension takes place in this phase. The hard phase may be broken down by the application of stress. Thus the fraction of rubber in each phase depends upon the previous history and the maximum stress to which the rubber has been subjected. At a given overall extension the strain existing locally in the soft regions depends upon the fraction of rubber which is present in this phase.

Before the initial extension of a filler reinforced vulcanizate the fraction of rubber in the soft phase is small and thus, at least at low extensions, the strain in the soft regions is considerably higher than the measured extension. As a result crystallization will occur at much lower overall extensions than in a corresponding gum vulcanizate. After a previous high extension the fraction of rubber in the soft phase will be greater and at a given overall extension the strain in the soft regions reduced proportionately, thus crystallization will not occur until a higher overall extension is reached.

Comparison of Figures 2 and 4 which show the effect of previous extensions of the black natural rubber vulcanizate on (a) the decrease in volume due to crystallization, and (b) the stress-strain behavior, indicates a strong parallelism in the dependence of both of these properties on previous extension. It adds confirmation to the hypothesis, which is implicit in the simple model discussed above, that both the upturn of the stress-strain curves and the onset of the decrease in volume with extension is due to some of the rubber being extended to sufficiently high strains so that (a) the finite extensibility of the chains in the molecular network contributes to the stress, and (b) the consequent orientation and alignment of the chains results in crystallization.

To put this description of the observed volume decrease on a quantitative basis would demand that allowance be made for the increase in volume due to the hydrostatic component of the applied force (including vacuole formation). In view of the uncertain approximations involved it is considered that such a quantitative treatment of the data is of limited value, and is not included here.

The behavior of the GR-S-black vulcanizate (Mix B) shown in Figure 3 is very different from that of the natural rubber-black vulcanizate. There is no evidence of a decrease in volume occurring at high extensions, and thus the data confirm that no crystallization occurs during extension. In contrast the

stress-strain curves in Figure 5 show similar behavior to that of the natural rubber-black vulcanizate.

Comparison of the curves in Figure 6 which give the increase in volume at low extensions with natural rubber peroxide and sulfur gum vulcanizates, confirms the extra increase in volume with the sulfur vulcanizate due to the formation of vacuoles around particles of zinc oxide. With the carbon black vulcanizate which also contains 5 parts of zinc oxide per hundred rubber there is no further large increase in volume even though it contains 50 parts of carbon black, and it thus appears that there is little or no vacuole formation around the carbon black particles.

The increase in stiffness which results from the incorporation of carbon black into rubber vulcanizates has frequently been described in terms of bonds between rubber and filler particles acting as additional crosslinks<sup>6,7</sup>. Recently attempts have been made to provide a quantitative basis for the stiffness of filler reinforced vulcanizates and the softening which results from previous

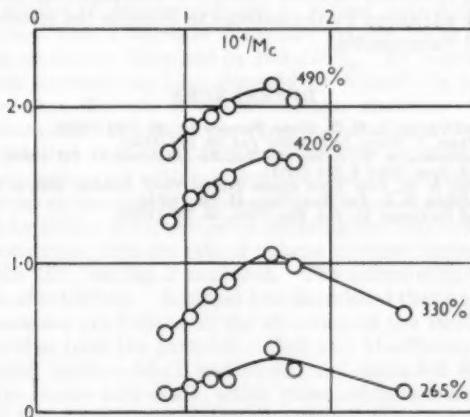


FIG. 7.—Dependence of change in volume with extension on degree of crosslinking (Morrell and Stern).

stretching in terms of the formation and breakdown of these additional crosslinks. The implications of the measurements described in this paper on such theories can now be discussed.

Morrell and Stern<sup>2</sup> have examined the effect of degree of crosslinking on the volume changes occurring during extension, and have shown that at any given extension the volume changes first increase and then decrease with increasing degree of crosslinking. Figure 7 gives their results for a range of natural rubber gum vulcanizates.

The degree of crosslinking necessary to give a natural rubber gum vulcanizate of similar stiffness at low extensions, to that of the carbon black vulcanizate before previous stretching, would be considerably greater than the most highly crosslinked vulcanizate used by Morrell and Stern. This is far beyond the maxima of the curves given in Figure 7, and thus, it is to be expected that breakdown of crosslinks in such a gum vulcanizate would result in an increase in the amount of crystallization at a given extension. The effect of previous

stretching of the black vulcanize on degree of crystallization, shown in Figure 2, is precisely opposite to this. Thus, the use of a highly crosslinked gum rubber in which some of the crosslinks break down during stretching as a model for carbon black filled vulcanizates is inconsistent with the crystallization data presented here.

#### ACKNOWLEDGMENT

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#### SUMMARY

The changes in volume which occur during the stretching of carbon black reinforced vulcanizates have been measured, and the results used to examine crystallization which accompanies the extension of natural rubber. The effect of previous extension on these changes is interpreted in terms of a simple model previously advanced by the authors to describe the stress-strain properties of reinforced vulcanizates.

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## CHANGES IN THE SPECIFIC VOLUME OF RUBBER DURING ELONGATION \*

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The study of volume changes in strained rubber not only has a practical significance, but is of considerable theoretical interest as well. Experimental data obtained from such measurements may be used to evaluate the structural changes which take place during the deformation and the nature of the forces involved in this process.

The first studies of volume changes in rubber were apparently those of Joule<sup>1</sup>, who found that a decrease in specific gravity by as much as 0.2% is observed when stocks are elongated by 100–150%. An increase in the volume of rubber when strained was also observed by Villari<sup>2</sup>; he found that as the elongation increases, the rate of volume increase slackens. Thomas<sup>3</sup>, in contrast to the others, did not note any increase in the volume of the rubber during elongation. Whitby<sup>4</sup> notes that this may possibly be explained by the fact that Thomas experimented with samples which had been previously deformed. Lundal<sup>4</sup> observed an increase in volume of as much as 0.45% when the rubber was elongated by 23%. Schippel<sup>5</sup>, after studying the behavior of loaded stocks, came to the conclusion that the rate of volume increase during elongation rises markedly as the filler loading is increased. The nature of the filler also affects the magnitude of this effect. Schippel first postulated that when a rubber stock is strained, vacuoles are formed in the direction of the strain by the tearing away of the rubber from the particles. Holt and MacPherson<sup>6</sup> carried out research on loaded (carbon black and chalk) and unloaded stocks. With the exception of the stocks with chalk, which increased in volume when elongated, the volume of the other stocks remained constant for elongations of 200% to 300%. Above this range the volume decreased; and the higher the elongation, the lower the temperature and the longer the period of time that the rubber remained in the strained condition, the greater was the amount of volume decrease. An increase in the degree of vulcanization generally diminishes the change in volume during elongation. The change in volume during these experiments was as high as 2%.

Gee, Stern and Treloar<sup>7</sup> made a study of the volume changes during elongation in natural rubber vulcanizates completely lacking in filler particles or any other rubber-insoluble particles; they found that upon elongation up to 100% the volumes increased by 0.01–0.02%. A correlation was noted here between the curves of volume ( $V$ ) versus elongation ( $\epsilon$ ) and of stress ( $\sigma$ ) versus elongation ( $\epsilon$ ). The increase in volume was attributed by the authors to the hydrostatic pressure created by strain in any isotropic body. By knowing the compressibility of the material and the degree of elongation one may calculate the increase in volume. Making such a calculation for both samples, the authors obtained values close to the experimental values.

\* Translated by Malcolm Anderson from *Kolloidnyi Zhurnal*, Vol. 19, pages 587–91 (1957).

The task of the present work was: (a) to study the change in volume of synthetic rubber stocks during elongation, which had never been studied before; (b) to carry out tests at high deformations; and (c) to try to find a correlation between stress and volume change during deformation.

The method of measurement chosen was basically the hydrostatic method of weighing, similar to that used by Gee, Stern and Trelaor<sup>1</sup>.

Rings with an inner diameter of 25 mm and an outer diameter of 28 mm were cut out of slabs of vulcanized rubber stock with a stamping die. Holes were drilled in a special steel plate, into which small steel rods were inserted various distances apart. The rings of rubber were stretched over the steel rods on either side of the strip. In this way it was possible to achieve elongations of 0% to 700% or more, in intervals of 50%. The device with the samples on it was weighed on an analytical balance in air and in distilled water with the samples at varying elongations, starting from zero. The change in volume was calculated from these data. All the necessary measures were taken to insure a constant temperature and to obtain reproducible results. In order to give a better wetting of the plate and free it from air bubbles, several drops of ethyl

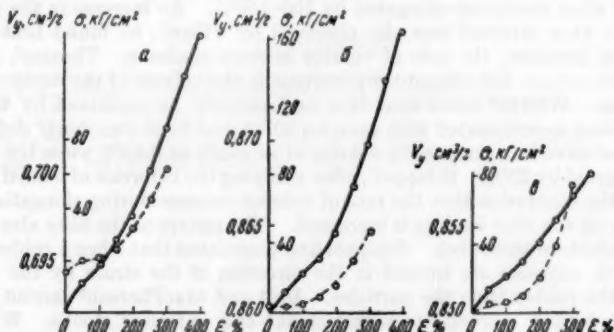


FIG. 1.—Relation of stress and specific volume to elongation in stocks based on: a (left)—chloroprene rubber; b (middle)—butadiene-styrene rubber (SKS-30); c (right)—polybutadiene rubber. The solid lines represent stress, the broken lines specific volume. The abscissas represent the per cent elongation  $E$ ; the outer ordinates represent the specific volume  $V_g$  in  $\text{cm}^3/\text{gram}$ , the inner ones the stress  $\sigma$  in  $\text{kg}/\text{cm}^2$ .

alcohol were added to the water. The experiments were carried out with stocks based on natural, polybutadiene, butadiene-styrene, nitrile, chloroprene and butyl rubbers. Both unloaded stocks and stocks with different loadings of carbon black, in different states of cure, were studied. Stress-strain curves were obtained for all stocks tested, from parallel determinations made on dumbbell specimens punched out of the same slabs from which the rings for volume measurement were cut. The recipes of the rubber stocks tested were approximately standard recipes, and for this reason they are not given. The graphs show only the loadings of the fillers.

Tests have shown that when various rubbers are stretched, their volumes undergo an increase which in isolated cases is as high as 1.7–1.8% at the maximum elongations. The curve of specific volume versus elongation is characteristically S-shaped in the general case; the increase in volume per unit elongation diminishes at first, and then (when the inflection point of the curve is reached) the volume starts to rise sharply as the elongation increases further (see Figures

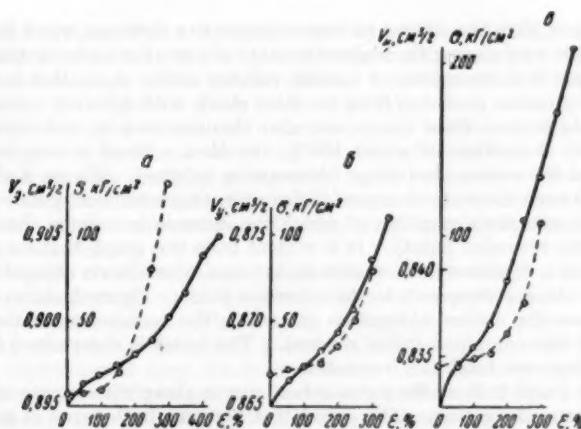


FIG. 2.—Relation of stress and specific volume to elongation in SKS-30 (butadiene-styrene rubber) stocks containing: a (left)—30 parts; b (middle)—45 parts; and c (right)—60 parts by weight of carbon black. The solid lines represent stress, the broken ones specific volume. The abscissas represent the elongation  $\epsilon$  in per cent; the outer ordinates represent the specific volume  $V_y$  in cm<sup>3</sup>/gram, the inner ones the stress  $\sigma$  in kg/cm<sup>2</sup>.

1 and 2). In some cases the S shape is not visible or only faintly visible, but in the majority of cases it is distinctly apparent. This is the case with stocks of all rubbers except natural rubber. When natural rubber is elongated to a

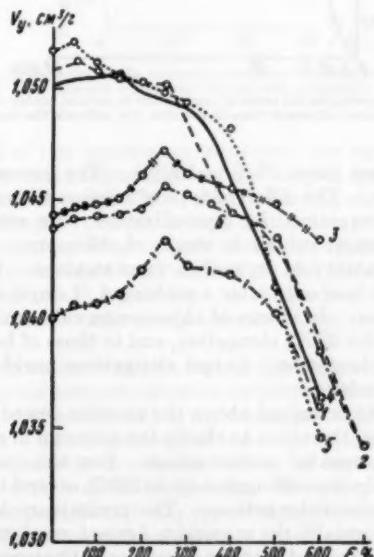


FIG. 3.—Relation between specific volume and elongation in natural rubber stocks vulcanized for periods of: 1—15 minutes; 2—30 minutes; 3—90 minutes; 4—10 minutes; 5—7.5 minutes and 6—6 minutes. The abscissa represents the per cent elongation  $\epsilon$ , the ordinate the specific volume in cm<sup>3</sup>/gram.

certain degree, then the volume increase changes to a decrease, which is slight at first and then very sharp; the higher the state of cure, the higher is this elongation. Figure 3 shows curves of specific volume versus elongation for natural rubber vulcanizates produced from the same stock, with different vulcanization periods. As is seen, these curves are also characterized by inflection points occurring at elongations of about 100%; but then a break occurs, indicating the start of the contraction stage (decrease in volume). Figure 4 shows the relation between the state of cure of the sample, characterized by its vulcanization period, and the elongation at which the increase in volume changes to a decrease (the reversion point). It is evident from this graph that for a certain state of cure, a 15 minute vulcanizate in our case, a maximum elongation value is reached which corresponds to the reversion point. Figure 5 shows the relation between the critical elongation (at which the contraction of the rubber starts) and the combined sulfur content. The latter is determined from the difference between total and free sulfur.

Figures 1 and 2 show the stress-strain curves along with curves of specific volume versus elongation. The correlation between both types of relation is quite evident. The inflection points of the respective curves correspond to the

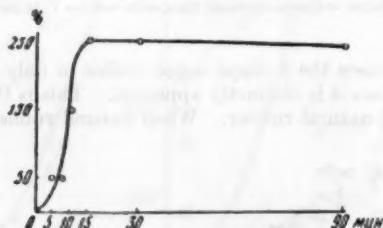


FIG. 4.—Elongation corresponding to the onset of contraction in natural rubber stock, as related to vulcanization time. The abscissa represents time in minutes, the ordinate the elongation  $\epsilon$  in per cent.

same elongation figures (from 75% to 150%). The curves shown are typical of most rubber stocks. The different type of relation shown by natural rubber stocks is apparently explained by crystallization. An attempt was made to bring about a decrease in volume in stocks of chloroprene and butyl rubbers, which also have the ability to crystallize when strained. However, a drop in volume was observed here only after a prolonged (7 days) aging of the sample in a strained condition. In stocks of chloroprene rubber the volume here decreased by 0.66% under 300% elongation, and in those of butyl rubber by only 0.09% under 250% elongation. Larger elongations could not be maintained for such long aging periods.

In the experiments described above the samples tested were not fatigued. It was of some interest, therefore, to clarify the behavior of rubber stocks previously subjected to repeated deformations. For this purpose ring-shaped samples cut out of slabs were elongated up to 300% several times and then were tested as usual at various elongations. The preliminary ten-cycle elongation almost always gave virtually the maximum figure for volume change.

These experiments showed that the character of the curves of volume versus elongation in such fatigued rubber parts remains unchanged, except that the rate of volume increase rises. Thus, when SKB (butadiene rubber) stocks were

elongated ten times, their volume increased by 0.04% to 0.15% in the range of elongations from zero up to 300%, as compared with samples not prestressed. SKN-26 (nitrile type rubber) stocks showed somewhat greater changes in the above range of elongations (from 0.4% to 0.7%).

It is interesting to note that in a comparatively few cases a second inflection point is observed in the curves of volume versus elongation, in the region of elongations near the breaking point, which indicates a gradual cessation of the increase in volume. An analogous inflection point can sometimes be observed also on the stress-strain curves in the region of large elongations, mainly in highly loaded stocks.

The results obtained leave no doubt that an increase in volume during elongation, continuing up to the point where the sample breaks, is a general property of vulcanizates. The drop in volume observed in natural rubber, beginning at a certain elongation, is due in all probability to crystallization—a process superimposed upon the main process. The volume increase observed can not, by reason of its magnitude, be due only to the hydrostatic component of the stress. It is very probable that during deformation a breakdown of the material occurs in the internal surfaces of the rubber itself, and at the rubber-filler particle surface. The possibility is not excluded, also, of a breakdown of the filler particles; i.e., that these are loosened up to form vacuoles within the

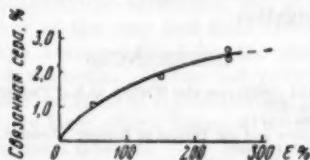


FIG. 5.—Elongation corresponding to the onset of contraction in natural rubber stocks, as related to the combined sulfur content. The abscissa represents the per cent elongation  $e$ , the ordinate the per cent combined sulfur.

particles. Not all of the occurrences mentioned are equally probable, but in the absence of accurate information on the subject one is compelled at the present time to speak in terms of the collective action of various factors.

One fact is noteworthy, however, and that is the presence of an inflection point on the curve of specific volume versus elongation, i.e., the S-shaped character of the curve. It would seem that the increase in volume during elongation should be steady by nature. A comparison of the inflection points on the curves of volume versus elongation and stress versus elongation is very interesting.

One might try to understand this fact on the basis of the assumption that a certain unstable spatial network exists in the stock, whose junctions are formed by secondary bonds of a different type, which are capable of breaking down during deformation. The breakdown of the network is accompanied by a drop in modulus and an increase in volume, because of increasing chain vibrations and the reduction of their steric hindrances. However, to the extent that the number of junctions capable of being ruptured decreases (the chains which are already oriented), the rate of volume increase should drop to its minimum value, corresponding to the inflection point of the curve. This also corresponds to the greatest decrease in modulus. A further increase in volume, one would think, might be due to still another mechanism, a component of the total

volume increase, which is the formation of vacuoles. This stage of deformation, incidentally, is usually characterized by a sharp rise in the hysteresis losses, indicating substantial structural disruptions.

The behavior of natural rubber definitely indicates that crystallization takes place during elongation. The decrease in volume in this case runs as high as 1.5% to 1.7%. It is characteristic that an increase in the state of cure, which reduces the distances between junctions, does not change, beyond a certain point, the per cent elongation at which crystallization commences. The more "free" the molecular chain is (i.e., the lower the state of cure), the more easily crystallization takes place.

### CONCLUSIONS

1. It was shown that an increase in volume under strain, which reaches 2% at the maximum elongations, is observed in both loaded and unloaded stocks based on different rubbers.

2. The curves of specific volume versus elongation are characteristically S-shaped in the general case, and the inflection points of these curves correspond to the same elongations as do the inflection points in the curves of stress versus elongation.

3. Natural rubber stocks show a drop in volume, related to the crystallization of the rubber, until a certain elongation is reached; the higher the state of cure, the higher this elongation.

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## CRYSTALLIZATION IN NATURAL RUBBER. V. CHEMICALLY MODIFIED RUBBER \*

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### INTRODUCTION

Small amounts of crosslinking have been shown to reduce the rate of crystallization of natural rubber by large factors<sup>1-4</sup>. It has also been inferred from measurements on peroxide and sulfur vulcanizates of various kinds that sulfur combined in forms other than crosslinks may retard the crystallization process efficiently<sup>2,3</sup>. A simple banned volume mechanism has been proposed<sup>3,4</sup> to account for the influence of crosslinking and sidegroup combination on the rate and final extent of crystallization, and has been shown<sup>4</sup> to predict the form of the observed dependences for crosslinked rubber, and approximately the relative magnitudes, but good quantitative agreement was not obtained. Measurements are described below of the rate and final extent of crystallization in natural rubber which has been modified by the chemical combination of sidegroups to the rubber molecule. It has not proved possible to account quantitatively for the observed rates of crystallization, but it is thought that a description of the extremely large effects found to accompany slight chemical modifications will be of general interest.

The preparation of the modified rubbers is described elsewhere<sup>5,6</sup>. The substances added were six thiol acids; namely, monochlorothiolic acid, trichlorothiolic acid, thiobenzoic, 1-thiolnaphthoic, thiolsalicylic, and thiol-stearic acids. The reactions were carried out in the solid phase by addition of the thiol acid to purified rubber on an open mill, in solution by addition of the thiol acid to a solution of purified rubber in benzene, and in the latex phase.

Ritter<sup>7</sup> has described temperature-retraction studies for similar modified rubbers and shown that the behavior is greatly altered. The crystalline state examined, however, appears to be a complex one, achieved in part during the imposition of a large extension and in part during a short period of storage of the extended testpiece at a low temperature. It seems unlikely therefore that any time-dependent processes which are observed correspond to a single crystallization process. Second, neither the retraction which is observed on releasing the extended testpiece nor the further retraction which occurs on warming can be readily related to the corresponding extent of crystallization. Finally, the experimental conditions, namely short periods of storage at a low temperature of samples held in a highly extended state, do not resemble those commonly encountered in arctic service—long periods of storage in the unstrained or lightly strained state—nor can the behavior under such conditions be deduced.

In the experiments which are described below the crystallization process has been followed dilatometrically<sup>1</sup> for unvulcanized samples in the unstrained state. In addition some measurements were carried out of the relaxation of

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stress in vulcanized samples held at a fixed extension in the range 0–200% extension<sup>3</sup>. The temperature at which the experiments were conducted was –25° C as this is close to the temperature at which crystallization proceeds most rapidly in raw and vulcanized rubber<sup>2,4,6</sup> and in vulcanizates stretched in the present range of extensions<sup>3</sup>.

### EXPERIMENTAL RESULTS

The rate of crystallization of natural rubber was found to be greatly reduced by the addition of thiol acids. The time functions describing the crystallization process were unchanged in form, however, and indicated the growth of spherical crystal structures from nuclei which appeared at a constant rate. Similar observations have been reported for crosslinked rubber<sup>4</sup>.

Some irreproducibility was evident in the products obtained by direct addition of the acid to rubber on an open mill. This was ascribed to inhomogeneous combination, since adding the acid in a dilute benzene solution and spreading it evenly over the exposed rubber surface yielded more slowly crystallizing modified rubbers similar to those obtained by reaction in solution, as is shown in Table I. The addition of thiol acids to latex yielded rubbers which crystal-

TABLE I  
CRYSTALLIZATION HALF-LIVES FOR MODIFIED RUBBERS

Amount of trichlorothiolic acid added to the rubber, %	Method of addition <sup>a</sup>	Crystallization half-life at –25° C min × 10 <sup>3</sup>
0	—	0.51
0.75	1	3.0
0.4	2	3.0
0.5	2	3.3
0.7	2	18.0
0.3	3	1.2
0.7	3	7.8
1.07	3	45.0

<sup>a</sup> (1) Acid added on mill. (2) Acid added as 5% solution in benzene on mill. (3) Acid added to 2% solution of rubber in benzene.

lized much more slowly at equivalent additions than modified rubbers prepared on an open mill or in solution.

At the low levels of addition employed, accurate analytical measurement of the amount of thiol acid which had combined proved impracticable, and the rubbers have therefore been characterized below by the amount of acid added.

In Figure 1, the observed crystallization half-lives for the modified rubbers prepared in solution are plotted on a logarithmic scale against the number of molecules of the thiol acids added to the rubber per unit volume. The experimental points are seen to be described approximately by linear relations, as predicted by the theoretical treatment<sup>4</sup>, although some tendency was discerned for the relatively highly modified rubbers to crystallize more slowly than a linear relationship would suggest. The relation obtained previously<sup>4</sup> for rubber cross-linked by means of an organic peroxide is represented by the broken line in Figure 1, the abscissa denoting the number of crosslinks per unit volume in this case. Thiolbenzoic, thiosalicylic, monochlorothiolic, and trichlorothiolic acids appear to be about equally effective in retarding the crystallization process, and somewhat more so than a corresponding number of peroxide cross-

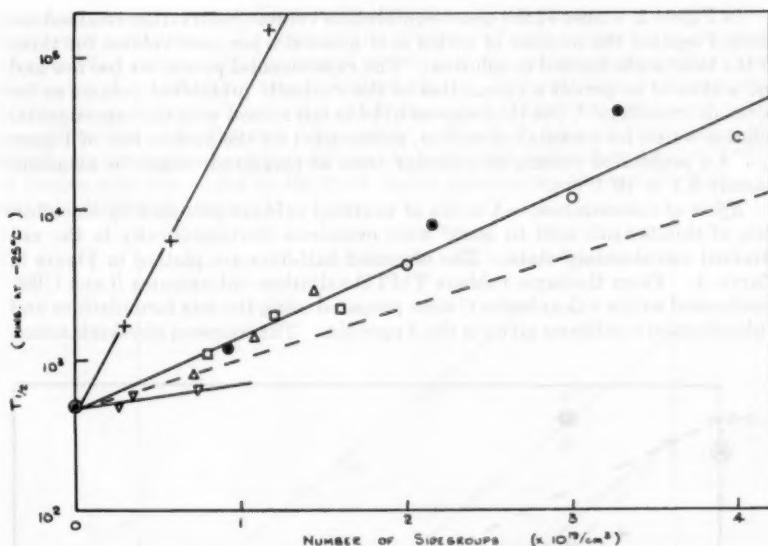


FIG. 1.—Experimental relations between crystallization half-life  $T_{1/2}$  at  $-25^\circ\text{C}$  and number of molecules of thiol acid per unit volume, added to the rubber in solution. (○) Monochlorothiolic acid; (●) trichlorothiolic acid; (□) thiobenzoic acid; (+) 1-thiolnaphthoic acid; (Δ) thiolsalicylic acid; (▽); thiostearic acid. The broken line represents the results obtained previously<sup>4</sup> on peroxide crosslinked rubber.

links. Thiolstearic acid was found to be considerably less efficient, only minor reductions in the rate of crystallization being observed for rubbers to which about  $10^{19}$  molecules per  $\text{cm}^3$  were added. 1-Thiolnaphthoic acid, however, was found to cause a greater reduction in the crystallization rate than any of the other acids examined, as is seen in Figure 1.

The efficiency of retardation for each additive may be characterized by the slope  $\partial(\ln T_{1/2})/\partial n$  of the corresponding linear relation of Figure 1. The experimental values are given in Table II, together with those obtained for modified rubbers prepared in the latex phase.

TABLE II  
EFFICIENCY OF THIOL ACID ADDITION IN RETARDING CRYSTALLIZATION

Additive	Method of addition*	Efficiency: $\partial(\ln T_{1/2})/\partial n$ $\times 10^{-20} \text{ cm}^3$	Effective excluded radius $\times 10^{-8} \text{ cm}$
Thiolstearic acid	3	ca 3	—
Monochlorothiolic acid	3	11	47
Trichlorothiolic acid	3	11	47
Thiobenzoic acid	3	11	47
Thiolsalicylic acid	3	11	47
1-Thiolnaphthoic acid	3	45	75
Peroxide crosslinks	—	7.4	41.5
Thiolstearic acid	4	7	—
Thiobenzoic acid	4	70–120	—
1-Thiolnaphthoic acid	4	120–190	—

\* (3) Acid added to 2% solution of rubber in benzene. (4) Acid added to latex.

In Figure 2, values of the quasi-equilibrium volume contraction attained are plotted against the number of added acid molecules per unit volume for three of the thiol acids reacted in solution. The experimental points are too few and too scattered to permit a calculation of the sterically prohibited volume as for peroxide crosslinks<sup>3,4</sup>, but they appear to be in fair accord with the experimental relation found for crosslinked rubber, represented by the broken line of Figure 2, and a prohibited volume of a similar order of magnitude might be assumed, namely  $5.1 \times 10^{-21} \text{ cm.}^3$ .

*Effect of vulcanization.*—A series of modified rubbers prepared by the addition of thiobenzoic acid to latex<sup>b</sup> were examined dilatometrically in the unstrained unvulcanized state. The observed half-lives are plotted in Figure 3, Curve A. From the same rubbers TMTD-sulfurless vulcanizates B and CBS-accelerated sulfur vulcanizates C were prepared using the mix formulations and vulcanization conditions given in the Appendix. The course of stress relaxation

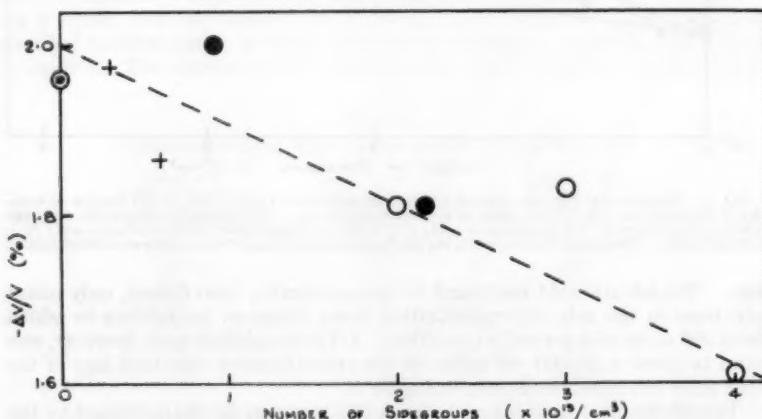


FIG. 2.—Experimental relation between quasi-equilibrium volume contraction at  $-25^\circ \text{C}$  and number of thiol acid molecules per unit volume, added to the rubber in solution. (○) Monochlorothiolic acid; (●) trichlorothiolic acid; (+) 1-thiophthalic acid. The broken line represents the results obtained previously<sup>4</sup> on peroxide crosslinked rubber.

in testpieces held at an extension ratio of 2.5 at  $-25^\circ \text{C}$  was then followed experimentally<sup>3</sup>. The observed half-lives for the stress relaxation process are plotted against the number of added sidegroups in Figure 3, Curves B and C, respectively. The retardation exhibited by the unstrained unvulcanized rubbers is seen to be present in the stretched vulcanizates, and the linear relations characterizing the measurements have approximately the same slope. The effect of sidegroup combination on the rate of crystallization appears, therefore, to be additional to, and independent of, the effect of crosslinking to a first approximation.

In a further series of measurements over a range of extensions, it was observed that an imposed extension increased the rate of crystallization for vulcanizates of modified and unmodified rubber by a similar factor.

*Effect of adding stearic acid.*—It has been shown previously<sup>8</sup> that the addition of small quantities of certain impurities, notably stearic acid, to purified rubber

increases the rate of crystallization fourfold at  $-25^{\circ}\text{C}$ , presumably by promoting crystal nucleation. To examine the efficiency of such impurities in chemically-modified rubbers, 2.5 per cent of stearic acid was added on an open mill to the series of modified rubbers described above. The resulting half-lives are portrayed in Figure 3, Curve A'. It is seen that the presence of stearic acid accelerates the crystallization by a factor of about five for all the degrees of modification examined. In an attempt to accelerate the process further, 10% of stearic acid was added to the most highly reacted sample, but the half-life was not further reduced.

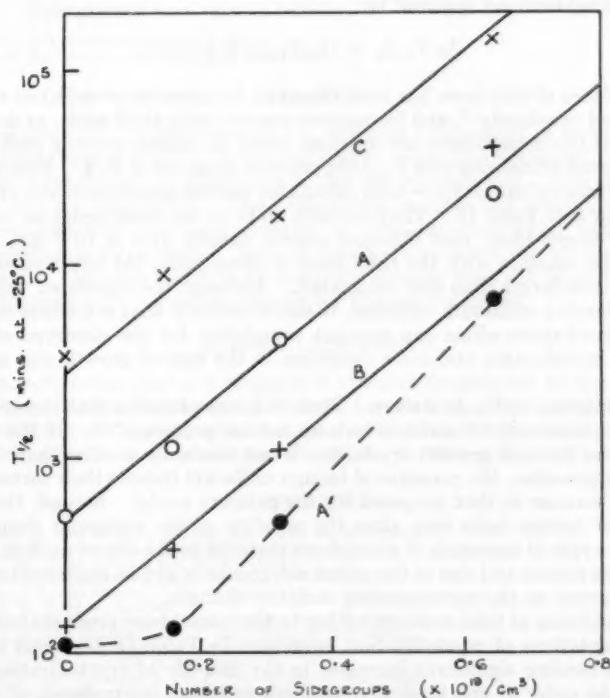


FIG. 3.—Experimental relations between crystallization half-life  $T_{1/2}$  at  $-25^{\circ}\text{C}$  and number of thiobenzoic acid molecules per unit volume, added to the rubber in the latex phase. (A) From dilatometric measurements on undeformed, unvulcanized rubbers. (A') From similar measurements on rubbers to which 2.5% of stearic acid was added on an open mill. (B) From measurements of stress relaxation in vulcanizates B, prepared from the same rubbers, held at an extension ratio of 2.5. (C) From similar measurements on vulcanizates C.

#### DISCUSSION

It has previously been proposed<sup>3,4</sup> that crosslinking and sidegroup addition retard crystallization by preventing the formation of crystal nuclei within an elementary volume around each foreign unit. The banned volume may be considered to consist of two zones. The first, immediately around the foreign unit, is sterically prevented from entering a crystal lattice, and an estimate of

its minimum size may be obtained from the dependence of the final degree of crystallization on the number of foreign units, as described in Section 2. The outer zone arises from the finite critical size of the crystal nucleus, which may be calculated at any temperature from classical nucleation theory<sup>4</sup>. The total nucleus-excluded volume  $V$ , assumed spherical, will have a radius given by the sum of the radii of the sterically prohibited zone and of the crystal nucleus. The calculated value for the nucleus-prohibited radius obtained in this way is  $21.4 \times 10^{-8}$  cm.

The crystallization half-life  $T_{1/2}$  for a material containing  $n$  randomly distributed foreign groups per unit volume which exclude the formation of nuclei in their neighborhood is given<sup>4</sup> by:

$$(\ln T_{1/2})_n = (\ln T_{1/2})_0 + nV/4$$

A dependence of this form has been observed for peroxide crosslinked rubbers, as reported previously<sup>1,4</sup>, and for rubbers reacted with thiol acids, as described above. If the retardations are ascribed solely to crystal nucleus prohibition, the measured efficiencies  $\partial(\ln T_{1/2})/\partial n$  provide measures of  $V/4$ . Values of the nucleus-excluded radius have been calculated on this assumption and are given in Column 3 of Table II. They are seen to be of the same order as, but considerably larger than, that obtained above, namely  $21.4 \times 10^{-8}$  cm. Moreover, if the reaction with the thiol acids is incomplete, the effective excluded radii are even larger than that calculated. Although the calculated value may be considered a minimum estimate, it seems unlikely that a nucleus-excluded volume mechanism alone can account completely for the observed effect of chemical modification and some reduction in the rate of growth also must be inferred.

This might occur in two ways. First, it seems probable that the growth of a crystal proceeds by a series of sub-nucleation processes<sup>10,11</sup>. If the critical nucleus size for such growth crystallites is not markedly smaller than that for primary nucleation, the presence of foreign units will impede their formation in a similar manner to that proposed for the primary nuclei. Second, the introduction of foreign units may alter the mobility of the molecular chains, and reduce the rate of approach of amorphous material to the site of nucleus formation. The nature and size of the added sidegroups might be expected to have a large influence on the corresponding mobility changes.

The addition of thiol acids to rubber in the latex phase produces extremely large retardations of crystallization, as is seen in Table II, the most efficient additions causing significant increases in the half-life of crystallization when only of the order of one thiol acid molecule is added per molecule of rubber. It is difficult to visualize the mode of action of such a phenomenally effective process, particularly as a corresponding number of long-chain foreign groups produced by graft<sup>12</sup> or block<sup>13</sup> polymerization of methyl methacrylate with rubber were found to have no significant effect on the rate of crystallization.

It seems likely therefore that the addition of the thiol acids to latex is accompanied by other structural changes in the rubber which also act to retard crystallization. Alternatively, if preferential combination of the thiol acid occurs in the surface layer of the latex particle and such spacial inhomogeneity is preserved throughout subsequent processing, a marked reduction in the rate of crystallization might be expected, comparable to that which is observed in latex itself<sup>10,14</sup>, due to the effectively finely-divided state of the crystallizable component.

## APPENDIX

## FORMULATIONS AND VULCANIZATION CONDITIONS

	Compound B parts by weight	Compound C parts by weight
Rubber	100	100
Zinc oxide	5	5
Stearic acid	2	1
Sulfur	—	2.5
Phenyl-2-naphthylamine	—	1
TMTD <sup>a</sup>	4	—
CBS <sup>b</sup>	—	0.7
Vulcanization time (min at 140° C)	40	30

<sup>a</sup> TMTD = Tetramethylthiuram disulfide.<sup>b</sup> CBS = N-cyclohexylbenzothiazolesulfonylbenamide.

## SYNOPSIS

Measurements are described of the rate and final extent of crystallization at a temperature of -25° C in natural rubber which has been modified by the chemical combination of sidegroups to the rubber molecule. The substances added were six thiol acids. Their efficiencies in retarding crystallization are compared with that previously reported for peroxide crosslinking and with the value predicted by a simple banned volume treatment for crystal nucleus formation. They are found to be generally greater than the large value predicted theoretically. Possible reasons for this are discussed.

## ACKNOWLEDGMENTS

This work forms part of a program of research undertaken by the Board of the British Rubber Producers' Research Association. The samples of thiol acid modified rubber prepared in benzene solution and in the latex phase were provided by Dr. J. I. Cunneen and Dr. F. W. Shipley of these laboratories.

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## THE ROLE OF METAL OXIDES AS ACTIVATORS OF VULCANIZATION \*

M. FELDSTEIN, P. ORLOVSKY, AND B. DOGADKIN

The study of the role of activators of vulcanization has, until recently, proceeded in two directions, the first approach being concerned with a study of the possible replacement of zinc oxide by less rare metal oxides<sup>1</sup>. In recent years, as a result of wide usage of synthetic rubber for which the role of zinc oxide as an activator is less definite, data were obtained by several scientists indicating the possibility of decreasing the amount of zinc oxide in rubber mixes. Since data with the opposite meaning have also been obtained, the question of decreasing zinc oxide content or replacing it by other metal oxides has not been settled.

The second approach taken by research workers was concerned with the determination of the nature of the role of activators of vulcanization. There is wide spread opinion that metal oxides activate the action of vulcanization accelerators by transforming the latter into more soluble salt-like compounds. According to several scientists<sup>2,3</sup>, the formation of di- and polysulfide compounds by reaction of vulcanization accelerators with sulfur followed by decomposition to free sulfur is promoted by metal oxides. In later research this point of view was not experimentally proved<sup>4</sup>.

The role of metal oxides as activators is not limited only to the influence on the kinetic process of vulcanization. Stevens<sup>5</sup> pointed out that zinc oxide improves physical-mechanical properties of vulcanizates. In a number of papers<sup>6-9</sup>, the activating role of zinc oxide is related to its influence on the cross-linkage of rubber molecules. Details of the action of zinc oxide are given in a paper by Dogadkin and Beniska<sup>10</sup>. To our regret, there is no basis in these papers for comparing the properties of other metal oxides with zinc oxide as activators of vulcanization.

The present work, based on an idea of P. F. Badenkov, was undertaken for the purpose of comparative study of the activating effect and properties of the oxides of a number of metals as a function of the type of rubber, the vulcanization accelerator and the active fillers. The compounds studied were zinc oxide, magnesium oxide, calcium oxide and calcium hydroxide. The following results are for mixtures containing 5 parts of activator but this quantity is not always optimal. In several cases, 1 part MgO and 3 parts Ca(OH)<sub>2</sub> show more effective activity than 5 parts. This is explained by better dispersion of these oxides in rubber at lower concentrations. In the case of zinc oxide, a decrease of concentration does not influence the nature of the dispersion. (Figure 1 of the original Russian article contained photomicrographs illustrating this point.)

Figure 1 of this translation shows the change of the dynamic modulus of "rod" polymerized sodium butadiene rubber (SKB = synthetic rubber, butadiene) containing different metal oxides but no fillers. As can be seen in the

\* Translated from *Kauchuk i Resina*, 1957, No. 1, pages 22-31.

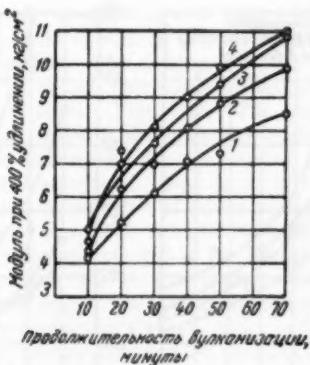


FIG. 1.—Vulcanization of rod polymerized sodium butadiene rubber in presence of Captax. Ordinate: modulus at 400% elongation, kg/cm<sup>2</sup>. Abscissa: vulcanization time, minutes. 1, without activator; 2, with calcium oxide; 3, with zinc oxide; 4, with magnesium oxide.

figure, the vulcanization effect increases when activators are present. An analogous effect is observed not only in the presence of mercaptobenzothiazole (Captax), but in the presence of other thiazole and sulfenamide accelerators, particularly with benzothiazolyl disulfide (Altax) and benzothiazolyl sulfendi-

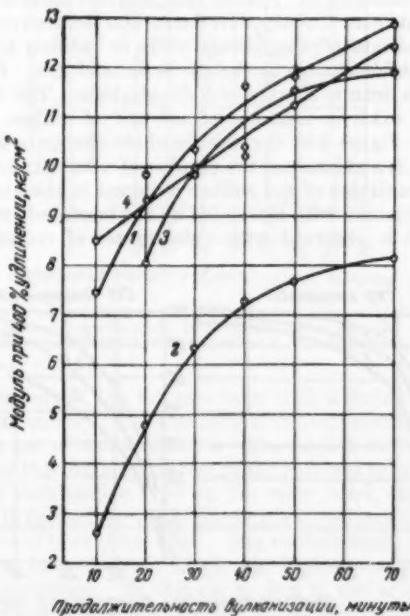


FIG. 2.—Vulcanization of rodless polymerized sodium butadiene rubber in presence of Captax. Ordinate: modulus at 400% elongation, kg/cm<sup>2</sup>. Abscissa: time of vulcanization, minutes. 1, without activator; 2, with zinc oxide; 3, with magnesium oxide; 4, with calcium hydroxide.

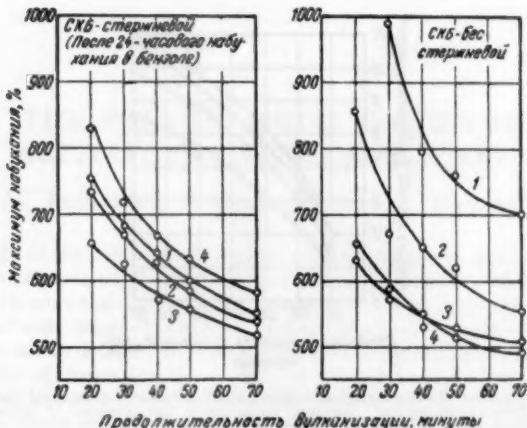


FIG. 3.—Kinetics of change of maximum swelling. Ordinate: maximum swelling, %. Abscissa: vulcanization time, minutes. Curve headings: left curve; SKB-rod (after 24 hours swelling in benzene); right curve; SKB-rodless 1, with zinc oxide; 2, with calcium oxide; 3, with magnesium oxide; 4, without activator.

ethylamide (Sulfenamide BT). Completely different results are observed on vulcanization of compounds of "rodless" polymerized sodium butadiene rubber (Figure 2). In this case the structure formation occurs very rapidly without metal oxides. Addition of magnesium oxide or calcium hydroxide does not produce an appreciable change in the dynamic modulus. In the presence of zinc oxide there is a definite slowing of vulcanization. The different nature of the action of zinc oxide in mixtures of rod and of rodless sodium butadiene rubber is shown in Figure 3 by the kinetics of the change in maximum swelling, which, as is known, is a measure of the number of crosslinks in the structure of a vulcanizate. Vulcanizates of rod rubber obtained in the absence of activator differ from those obtained with zinc oxide by the increased swelling in benzene. The opposite effect is observed with vulcanizates of rodless rubber; greater

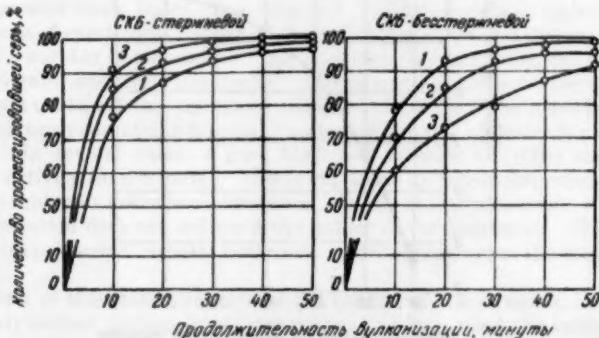


FIG. 4.—Kinetics of addition of sulfur. Ordinate: amount of sulfur reacted. Abscissa: vulcanization time, minutes. Left curve heading: SKB-rod; Right curve heading: SKB-rodless 1, without a rod; 2, with magnesium oxide; 3, with zinc oxide.

swelling is characteristic of vulcanizates with zinc oxide. This effect proves that zinc oxide in compounds of rodless sodium butadiene rubber slows the process of structure formation. The difference in the effect of zinc oxide in mixtures with rod and with rodless polymerized SKB can also be seen from the kinetics of the addition of sulfur (Figure 4). The quantity of sulfur bound means all the sulfur that stays in the vulcanizate after acetone extraction. This includes all organic combined sulfur and sulfur which is part of metal sulfides formed during vulcanization. Zinc oxide in rod rubber compounds causes greater acceleration of addition of sulfur than magnesium oxide. In rodless rubber compounds, zinc oxide retards the reaction of sulfur addition and the greatest acceleration is observed in the absence of metal oxides.

The above results show the different effects of zinc oxide in pigmented compounds of rod and rodless polymerized sodium butadiene rubber. In compounds of rodless rubber containing Captax, Altax and Sulfenamide BT, zinc oxide slows vulcanization, sharply lowering the speed of reaction of rubber with

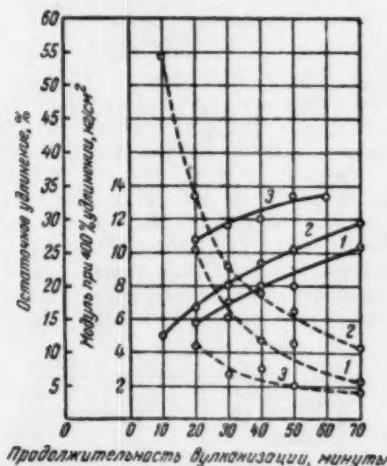


FIG. 5.—Vulcanization of rodless SKB (0.22% alkali) in the presence of Captax. Outer ordinate: residual elongation, %. Inner ordinate: modulus at 400% elongation, kg/cm<sup>2</sup>. — modulus, — residual elongation. 1, without activator; 2, with zinc oxide; 3, with magnesium oxide.

sulfur. For accelerators of the thiuram type such differences in the effect of metal oxides in compounds of rod and rodless rubber were not observed: both rubbers require the use of zinc oxide as a vulcanization activator. This gives us reason to suppose that for accelerators of the thiuram type on one hand, and of the thiazole and sulfenamide type on the other hand, there exist different activator effects. It depends not only on chemical composition of the accelerator but on the nature of the rubber used. The rubbers made in production may contain by-products, in particular, alkali, which shows considerable effect on the kinetics of vulcanization. In this connection it was of interest to explain the anomalous behavior of zinc oxide in rodless sodium butadiene rubber, particularly as to whether it depends on the type of rubber or on the presence of alkali. To answer this question, samples of rodless SKB were taken which

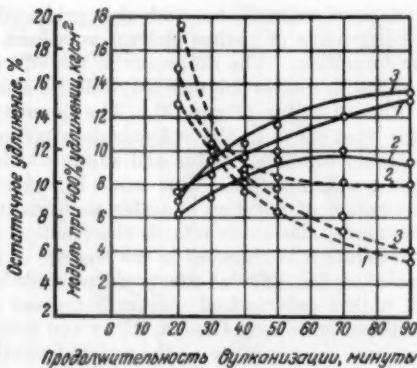


FIG. 6.—Vulcanization of rodless SKB (0.6% alkali) in the presence of Captax. Ordinate, abscissa and key the same as for Figure 5.

differed from each other by their alkali content. The alkali content of the first sample of rubber was 0.22 per cent expressed as sodium hydroxide. The second sample contained 0.6 per cent. Figure 6 gives the kinetics of the change in physical-mechanical properties of compounds of the rodless SKB containing 0.22 per cent alkali. From this it is seen that the vulcanizate with zinc oxide has a higher modulus and a higher residual elongation than the vulcanizate obtained without activator. The same effect was observed in the presence of Sulfenamide BT as in the presence of Captax (Figure 5). In other words, in rodless rubber with low alkali, the influence of zinc oxide is not clearly shown. When higher alkali content is present (0.6 per cent), the retarding action of zinc oxide on the vulcanization process is definitely shown (Figure 6). This

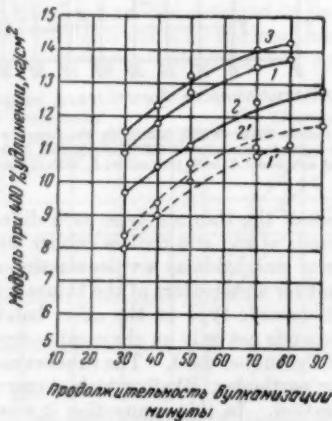


FIG. 7.—Effect of sodium hydroxide on vulcanization of rodless SKB (0.22% alkali). Ordinate: modulus at 400% elongation,  $\text{kg}/\text{cm}^2$ . Abscissa: vulcanization time, minutes. 1', without activator; 2', with sodium hydroxide; 3', with zinc oxide and sodium hydroxide.

is proved by the decrease in modulus and the increase in residual elongation. Figure 7 shows the effect of adding alkali to rodless SKB (the additional alkali was obtained by adding 3 parts of sodium hydroxide). As was shown in Figure 5, zinc oxide in rodless rubber with low alkali content (0.22 per cent), causes higher modulus than is obtained without metal oxide. Upon adding sodium hydroxide the vulcanizates with zinc oxide (Figure 7) have a lower modulus. From this we can conclude that with higher alkali content in the rubber, the addition of zinc oxide appears to be unnecessary for vulcanization of unpigmented compounds of rodless polymerized SKB.

This behavior of zinc oxide can be explained in the following manner. In the presence of a considerable amount of alkali the vulcanization proceeds rapidly without metal oxides. Moreover, at the temperature of vulcanization, the reaction of zinc salts with vulcanization accelerators and sulfur leads to the formation of zinc sulfide and therefore to the expending of part of the sulfur. In consequence, there is less immediate reaction between rubber and sulfur, resulting in a delay in vulcanization.

The characteristic effect of metal oxides as vulcanization activators depends to a considerable degree on the type of fillers used. As can be seen in Table I,

TABLE I  
ACTIVITY OF ACTIVATORS IN PIGMENTED COMPOUNDS OF SODIUM BUTADIENE RUBBER;  
50 MINUTE CURE AT 143°C; 1.5 PARTS SULFUR; 1.8 PARTS CAPTAX IN SKB RUBBER

Activator	Activator content, parts	Modulus at 300% elongation, kg/cm <sup>2</sup>					
		Filler					
		Channel black		Furnace black		Oil spray black	
No black	Black	No black	Black	No black	Black	No black	Black
Without activator		42	57	43	64	78	76
Zinc oxide	5.0	62	74	44	68	81	79
Zinc oxide	1.0	60	73	42	67	81	80
Magnesium oxide	3.0	52	62	44	72	85	80
Calcium hydroxide	3.0	56	62	46	66	80	78

the vulcanization of compounds of sodium butadiene rubber containing semi-active blacks (furnace black and "sprayed oil" black) proceeds intensively in the absence of metal oxides. Addition of metal oxides does not appreciably affect the rate of cure. The nature of the activity of metal oxides in the presence of active channel black is considerably different.

The influence of active channel black on vulcanization is so large that in a given case the difference between the behavior of activators in rod and rodless polymerized SKB is wiped out. For both types of rubber, addition of channel black requires the use of activators—metal oxides, of which the most active is zinc oxide.

The results obtained in studying the role of metal oxides in vulcanization of butadiene styrene rubber (SKS-30A) are of great interest. Here, the influence of metal oxides on the rate of vulcanization and on the process of structure formation and the specific action in the presence of different fillers was observed. The compounds studied contained the most effective accelerator for each type of rubber. The vulcanizates used contained sulfenamide BT, thiuram or Altax, and each contained diphenylguanidine (DPG). The effect of calcium hydroxide as an activator was compared with the normally used zinc oxide. Magnesium oxide is intermediate between the above metal oxides in its effect as an activator

of butadiene styrene rubber vulcanization. The effect of zinc oxide and calcium hydroxide on the rate of cure of nonpigmented compounds of SKS-30A containing Altax and DPG (0.6 part) is shown in Figure 8.

The results show that calcium hydroxide is more effective than zinc oxide with respect to rate of cure and structure formation as measured by modulus. Analogous results are observed in vulcanizates of compounds containing Sulfenamide BT. Curves of rate of addition of sulfur (Figure 8) show that the compounds of SKS containing thiazole accelerators vulcanize rapidly enough without vulcanization activators. Such a compound, after 30–40 minutes of cure (in other words, up to the optimum cure), contains as much bound sulfur as compounds containing activators, zinc oxide or calcium hydroxide. However, as measured by modulus and tensile strength (Figure 8), compounds without activators are far less advanced in cure than the ones containing metal oxides. The modulus values show that with practically the same amount of sulfur reacted, a considerably greater structure formation is obtained in the presence

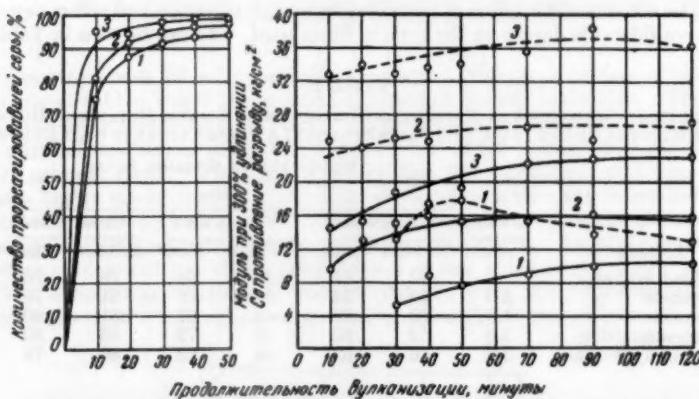


FIG. 8.—Vulcanization of butadiene styrene rubber in presence of Altax and diphenylguanidine. Left ordinate: Amount of reacted sulfur, %. Right ordinate: modulus at 300% elongation, tensile strength, kg/cm<sup>2</sup>. Abscissa: vulcanization time, minutes. — modulus; —— tensile strength. 1, without activator; 2, with zinc oxide; 3, with magnesium oxide.

of metal oxides. In this manner activators, like accelerators, cause better utilization of sulfur and influence the nature of the vulcanizate structure. In this respect, calcium hydroxide is much more effective than zinc oxide.

We should mention that vulcanizates obtained by the use of calcium hydroxide are approximately one and one-half times as high in tensile strength as those obtained with zinc oxide.

The addition of semi-active fillers, such as furnace black, to butadiene styrene rubber does not cause appreciable changes in the effect of activators described for nonpigmented compounds with the above mentioned types of accelerators.

In compounds with channel black, Altax and DPG (Figure 9), calcium hydroxide appreciably surpasses zinc oxide as an activator. In the presence of Sulfenamide BT the action of zinc oxide and calcium hydroxide as activators is practically identical. However, we should keep in mind that the effect of

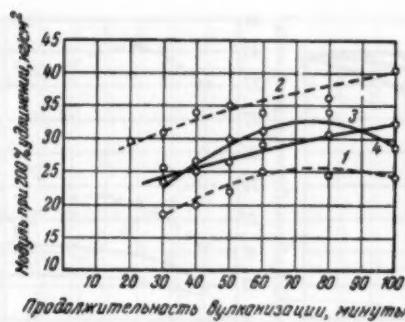


FIG. 9.—Activity of accelerators in compounds of SKS-30A containing channel black, as a function of the type of accelerator used. Ordinate: modulus at 200% elongation, kg/cm<sup>2</sup>. Abscissa: vulcanization time, minutes. — Altax, DPG (0.75 part); - - - Sulfenamide BT (1 part). 1,3. with zinc oxide; 2,4. with calcium hydroxide.

activators depends on the concentration of accelerators to a certain degree. Figure 10 gives the results which characterize the influence of metal oxides on the physical-mechanical properties of compounds with channel black containing varying amounts of Sulfenamide BT. At a concentration of 1.2 phr of Sulfenamide BT, zinc oxide and calcium hydroxide exhibit practically the same activation effect as shown above. On decreasing the concentration of Sulfenamide BT to 0.7 part, where the role of activators sharply increases, calcium hydroxide has a greater activity effect and causes greater structure formation.

It is known that thiuram in compounds with natural rubber or with SKB, rod or rodless polymerized, is activated exclusively by zinc oxide. Oxides of other metals appear to be weak activators. A difference is observed with vulcanization of butadiene styrene rubber in the presence of thiuram. As is seen in Figure 11 showing the rate of vulcanization of nonpigmented compounds of butadiene styrene rubber (SKS-30A), calcium hydroxide in the presence of thiuram causes greater acceleration of sulfur addition and gives higher modulus values and higher tensile strength than is obtained with zinc oxide. Addition

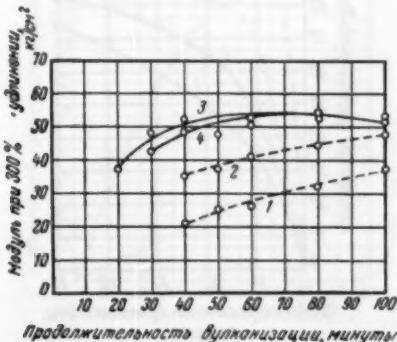


FIG. 10.—Effect of activators as a function of accelerator concentration. Ordinate: modulus at 300% elongation, kg/cm<sup>2</sup>. Abscissa: vulcanization time, minutes. — Sulfenamide BT (1.2 parts); - - - Sulfenamide BT (0.7 part) 1,3. with zinc oxide; 2,4. with calcium hydroxide.

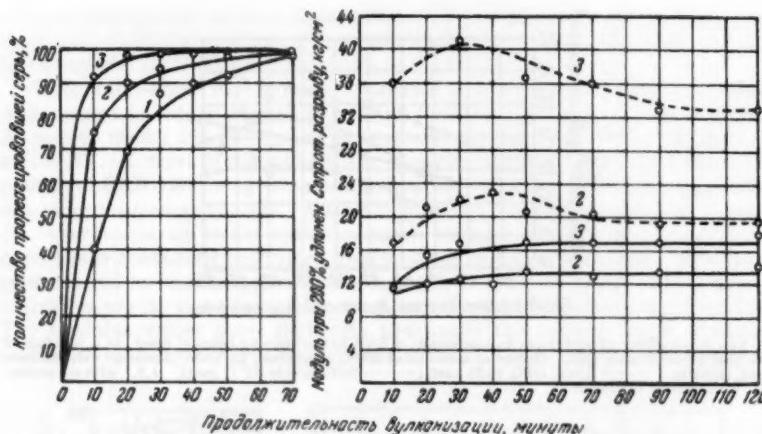


FIG. 11.—Vulcanization of butadiene styrene rubber in the presence of thiuram. Left ordinate: amount of reacted sulfur, %. Right ordinate: modulus at 200% elongation, tensile strength, kg/cm<sup>2</sup>. 1, without activator; 2, with zinc oxide; 3, with calcium hydroxide.

of furnace black (Figure 12) does not affect the activity of this activator. In compounds of thiuram with channel black, the activity is weaker with calcium hydroxide than with zinc oxide as vulcanization activator. The latter causes greater acceleration of sulfur addition (Figure 12). The vulcanizates obtained by the use of calcium hydroxide are characterized by low tensile strength: 70–80 kg/cm<sup>2</sup>, against 250 kg/cm<sup>2</sup> for vulcanizates with zinc oxide. Such a decrease in tensile strength is probably due to the reactivity of calcium hydroxide with functional groups containing oxygen which are on the surface of channel black.

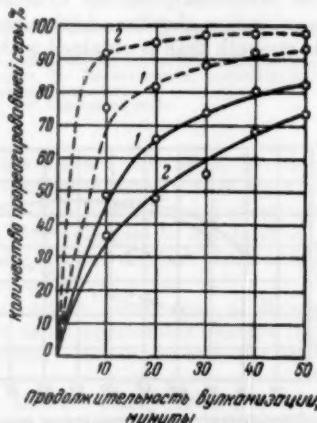


FIG. 12.—Effect of activators in compounds of SKS-30A containing thiuram as a function of the type of filler. Ordinate: amount of sulfur reacted, %. Abscissa: vulcanization time, minutes. — with channel black; - - - with furnace black. 1, with zinc oxide; 2, with calcium hydroxide.

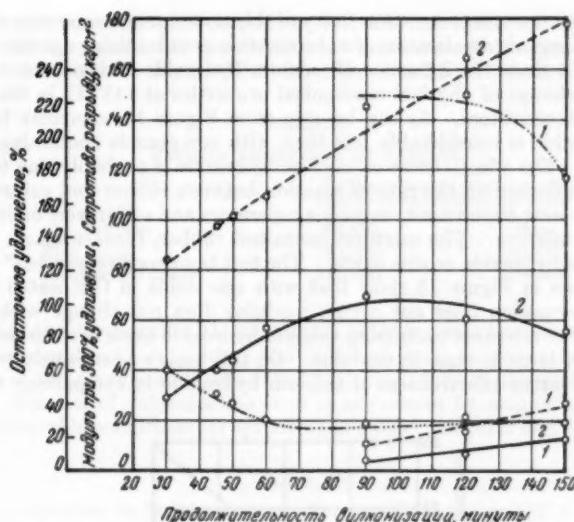


FIG. 13.—Structure formation effect of metal oxides in the absence of accelerators (in furnace black compounds). Outer ordinate: residual elongation, %. Inner ordinate: modulus at 300% elongation, tensile strength, kg/cm<sup>2</sup>. Abcissa: vulcanization time, minutes. — modulus; —— tensile strength; - - - residual elongation. 1, with zinc oxide; 2, with calcium hydroxide.

The experimental data described above show that in all compounds of butadiene styrene rubber studied, with the exception of those using thiuram and channel black, calcium hydroxide possesses stronger activity than zinc oxide.

For the purpose of study of the basis for the special effectiveness of calcium hydroxide with respect to SKS rubber, we obtained additional data which

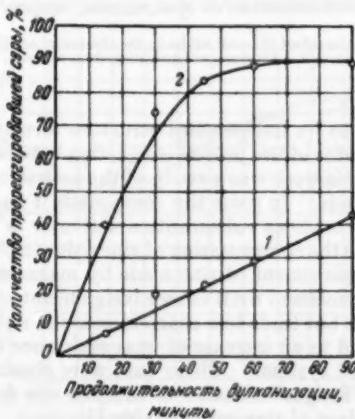


FIG. 14.—Influence of metal oxides on rate of sulfur addition (in absence of accelerators). Ordinate: amount of reacted sulfur, %. Abcissa: vulcanization time, minutes. 1, with zinc oxide; 2, with calcium hydroxide.

characterized the vulcanization activity of this material in compounds which did not contain organic accelerators of vulcanization or vulcanizing agents. Curves in Figure 13 show the influence of calcium hydroxide and zinc oxide on the kinetics of change of physical-mechanical properties at 143° C, in the absence of organic accelerators. As can be seen from Figure 13, structure formation with zinc oxide is considerably less than with compounds containing calcium hydroxide. The effectiveness of calcium hydroxide is probably due to the accelerating influence on the rate of reaction between rubber and sulfur (Figure 14). In the next experiment, organic accelerators and sulfur were omitted from the rubber mixture. The mixtures contained rubber, furnace black, softener, and calcium hydroxide or zinc oxide. The test temperature was 143° C. The results shown in Figure 15 show that with zinc oxide in the heated mixture, structure formation does not occur; modulus does not change with time of heating. For mixtures containing calcium hydroxide there is observed a linear but not very large increase in modulus. On this basis we can conclude that the special activation effectiveness of calcium hydroxide in comparison with zinc

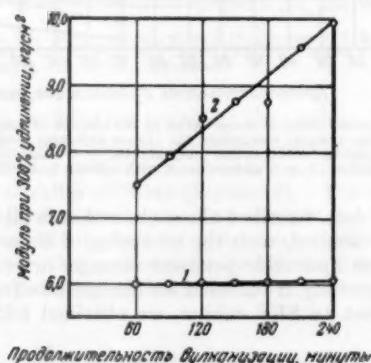


FIG. 15.—Structure formation effect of metal oxides in the absence of accelerator and sulfur. Ordinate: modulus at 300% elongation, kg/cm<sup>2</sup>. Abcissa: vulcanisation time, minutes. I, with zinc oxide; Z, with calcium hydroxide.

oxide is due, in part, to its independent structure formation activity and its influence as an accelerator of the process of reaction between rubber and sulfur.

The next topic of this work was a study of the activity of activators in various industrial compounds. In some tire compounds it has been found expedient to add magnesium oxide as vulcanization activator in place of zinc oxide; also to greatly decrease the concentration of zinc oxide in other compounds. It was found that the replacement of zinc oxide by magnesium oxide in breaker compounds of rod polymerized SKB causes insignificant changes in the indicators of wear resistance, but leads to a sharp increase of resistance of the rubber to repeated flexing, and to an increase of wear resistance of multilayer plies of rubber and rubber cord systems. These data were obtained with the help of G. A. Levitina. The fatigue resistance of samples was doubled by the use of magnesium oxide in place of zinc oxide (Table II).

The other important property of magnesium oxide is that in its presence there is less tendency toward premature vulcanization (Table III).

In the above mentioned compounds with SKB, magnesium oxide, in comparison with zinc oxide, causes a delay of vulcanization at the beginning of the process. As shown in Figure 16, during the first 20–30 minutes of cure the

TABLE II  
FATIGUE RESISTANCE OF SAMPLES

Activator	Fatigue resistance of rubber cord samples on repeated flexing, cycles	
	Bending	Shear
Zinc oxide	171,000	255,000
Magnesium oxide	382,000	270,000

modulus of the compound with magnesium oxide is lower than that of the zinc oxide compound, and only when the optimum cure is approached does the modulus of the magnesium oxide compound equal that of the zinc oxide compound. Kinetics of vulcanization such as are caused by magnesium oxide results in favorable conditions for spreading of rubber mixtures and for adhesion,

TABLE III  
CHANGE OF PLASTICITY WITH TIME OF HEATING AT 110° C

Compound	Activator	Plasticity (Goodrich plastometer)			
		Time of heating, minutes			
		5	15	30	50
Breaker compound, rod SKB	Zinc oxide	0.72	0.70	0.31	0.00
	Magnesium oxide	0.73	0.74	0.68	0.50

which, in the case of multilayers, leads to obtaining a product with increased stability of bonds between plies<sup>11</sup>.

Therefore, the use of magnesium oxide in compounds of SKB (particularly in breakers) protects the compound before vulcanization, causes more favorable

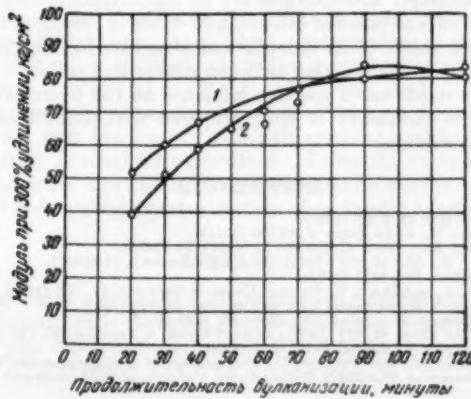


FIG. 16.—Dynamics of change of modulus of breaker compounds of SKB. Ordinate: modulus at 300% elongation, kg/cm<sup>2</sup>. Abcissa: vulcanization time, minutes. 1, with zinc oxide; 2, with magnesium oxide.

kinetics of vulcanization and shows a positive influence on fatigue life. On this basis we can expect that the presence of magnesium oxide in tire compounds will favorably influence the durability of tires. Certainly the results of machine testing of tires (Table IV) of size 210-20 with magnesium oxide in the breaker

TABLE IV  
RESULTS OF MACHINE TESTING OF TIRES

Size	Sample type	Rolling condition	Average run on machine, km	
			Experimental	Control
210-20	Zinc oxide in breaker replaced by magnesium oxide	Speed, 40 km/hr, 9.5 mm cleat	11,440	5389
260-20	Same as above	The same	3126	3103
260-20	MgO in breaker and 2 parts ZnO (instead of 5)	The same	5809	3103
200-20	Same as above	50 km/hr, 20 mm cleat	3480	1700

compound and tires of size 260-20 with the same breaker compound and with less zinc oxide in the tread, shows that this change of recipe leads to an increase in durability of the tires.

#### CONCLUSIONS

1. The activation effect of metal oxides on the process of vulcanization of nonpigmented compounds of rod polymerized sodium butadiene rubber differs from the effect in rodless polymerized rubber. In the latter case zinc oxide not only is not an activator but it retards the vulcanization process.
2. The role of activators depends, to a large degree, on the type of vulcanization accelerator and active filler used.
3. Metal oxides increase the amount of structure formation in the vulcanizate.
4. With regard to butadiene styrene rubber (SKS-30A), calcium hydroxide appears to have stronger activating effect on vulcanization than zinc oxide.
5. The special effectiveness of calcium hydroxide in compounds of butadiene styrene rubber is a result of its independent structure forming ability and accelerating influence on the reaction between rubber and sulfur.
6. Magnesium oxide has a positive influence on the technical properties of rubber and on the durability of tires prepared with butadiene styrene and sodium butadiene rubbers.

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## VULCANIZATION OF ELASTOMERS. 14. ROLE OF THE OXIDE IN VULCANIZATION WITH COMPOUNDS OF THE THIURAM SERIES. I \*

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### INTRODUCTION

In a paper<sup>2</sup> appearing shortly, the experimental part of which deals with the vulcanization of Perbunan with tetramethylthiuram monosulfide (TMTM) and sulfur (S) (TMTM:S = 1:1), the mechanism of the thiuram vulcanization will be considered generally and attempts will be made to explain results of previous kinetic investigations. In that paper discussions of the probability of an intermediate compound entering into the vulcanization play a special role. This paper reports studies whose results indicate as far as possible the origin of the intermediate compound and which emphasize the obviously absolute necessity of zinc oxide for thiuram disulfide vulcanization. We have previously made investigations from which it may be concluded that the vulcanization reaction takes place in contact with zinc oxide<sup>3</sup>. Still the influence of both the thiuram disulfide concentration and the zinc oxide content of the mixtures on the kinetics of thiuram disulfide vulcanization has not been worked out quantitatively. That can be done with the results given in this paper.

We have described the preparation of the thiuram vulcanizates in former publications and in them have reported fully on the quantitative analysis of the vulcanizate extracts<sup>4</sup>. Therefore, it is unnecessary to discuss the techniques since they were used with no essential changes for the work in this paper. The present results treat the kinetics of the thiuram disulfide vulcanization of natural rubber and Perbunan at (1) constant concentration of thiuram disulfide with increasing zinc oxide addition, (2) varying content of a mixture of zinc oxide and thiuram disulfide at constant molar ratio, and (3) constant zinc oxide content and self-changing concentration of thiuram disulfide.

All experiments were carried out with pale crepe as well as with Perbunan 2818 (both carefully purified by extraction). From the work with Perbunan 2818 especially accurate and highly informative results were obtained, possibly a consequence of only unimportant variation of molecular nature on milling.

### RESULTS

When one maintains a constant concentration of tetraethylthiuram disulfide (TETD) in Perbunan while increasing successively the content of zinc oxide, then the limit of zinc dithiocarbamate (ZnDED<sub>C</sub>) formation remains unaltered at 66 mole% of TETD used<sup>5</sup>, and both the decrease of TETD concentration

\* Translated by Seward J. and Mary B. Averill for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi*, Vol. 10, pages WT109-115, May 1957. The seven tables in the original have been omitted. See Reference 1 for Paper 13.

and the formation of ZnDEDC can be described in each case by first order kinetics. The TETD decrease is always the faster reaction.

Figure 1 shows the ZnDEDC formation (left) and the TETD decrease (right) to be first order reactions at increasing additions of zinc oxide and constant concentration of TETD (10 millimoles per 100 g complete mixture). One recognizes immediately that an increase in zinc oxide content results in an increase in slope for the kinetic plots in the series A to H. In other words, the velocity constants of both TETD decrease and ZnDEDC increase rise with increasing zinc oxide content of the mixture.

If one calculates, by means of data compiled in Tables I and II and through utilization of curves in Figure 1, the velocity constants of TETD decrease,  $k_{TD}$ , and of ZnDEDC increase,  $k_{DC}$ , (see Table VII, No. 1-8) and plots them

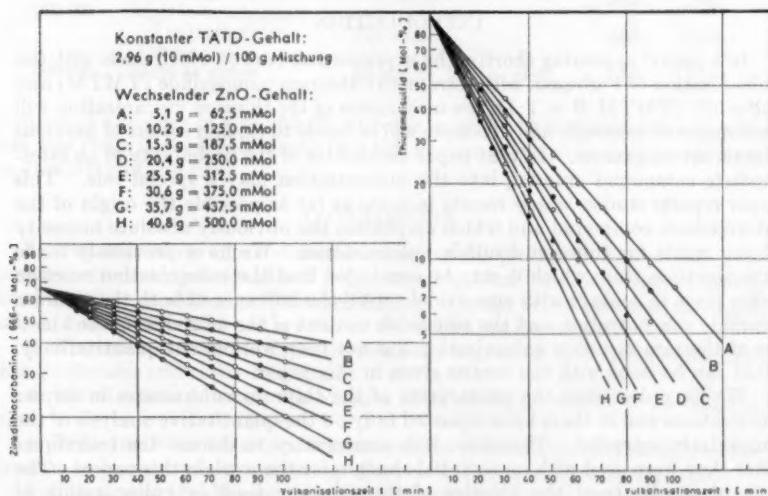


Fig. 1.—Progress of TETD decrease and ZnDEDC increase according to first order kinetics in vulcanization of Perbunan 2818 with TETD: TETD concentration constant, zinc oxide content rising A to H. Vulcanization temperature 120° C.

as a function of the zinc oxide content (millimoles or g in 100 g of mixture), then there results, as Figure 2(1) shows for both velocity constants, a linear dependence which can be written as follows:

$$k_{TD} = \%k_{TD}^I + \%k_{TD}^I a [ZnO] \quad (1)$$

$$k_{DC} = \%k_{DC}^I + \%k_{DC}^I b [ZnO] \quad (2)$$

In the equations  $\%k_{TD}^I$  and  $\%k_{DC}^I$  mean the velocity constants of TETD decrease and of ZnDEDC formation for  $[ZnO] = 0$ , and  $a$  and  $b$  are constants—that is, the increase of the velocity constants  $k_{TD}^I$  and  $k_{DC}^I$  brought about by a unit quantity of  $[ZnO]$ . The constant  $a$  is dependent upon the TETD concentration, i.e.,  $a = f[TETD]$ . One observes that  $\%k_{TD}^I$  and  $\%k_{DC}^I$  are not experimental quantities, rather, they are the ordinate intercepts of both lines in

Figure 2(1)<sup>6</sup>. From Equations (1) and (2) one obtains for the constants

$$a = \frac{(k_{TD}^I - \% k_{TD}^I)}{\% k_{TD} [\text{ZnO}]} \quad (3)$$

$$b = \frac{(k_{DC}^I - \% k_{DC}^I)}{\% k_{DC} [\text{ZnO}]} \quad (4)$$

Figure 3 shows the kinetics of TETD decrease and ZnDEDC increase under the condition that the TETD concentration and the zinc oxide content of the mixture are altered simultaneously so that the molar ratio [ZnO]:[TETD] remains constant. In the present case it amounts to 12.5. One sees that

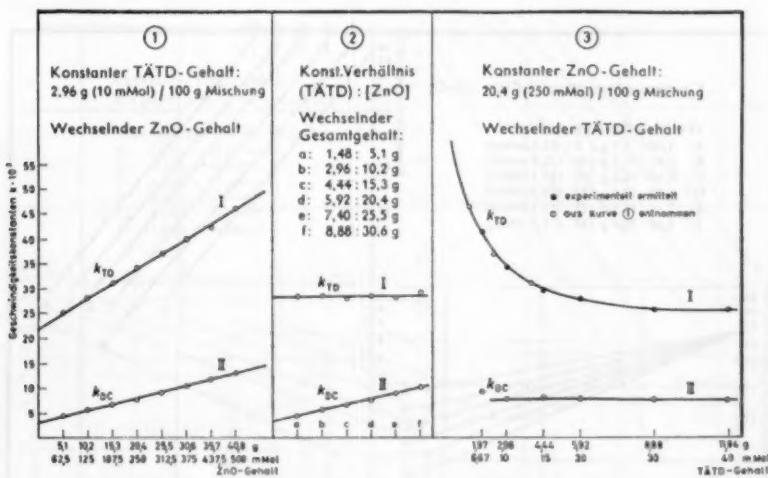


FIG. 2.—Variation in velocity constants of TETD decrease,  $k_{TD}^I$ , and of ZnDEDC increase,  $k_{DC}^I$ , as it depends upon zinc oxide content and TETD concentration in vulcanization of Perbunan 2818 with TETD at 120° C. (1):  $k_{TD}^I$  and  $k_{DC}^I$  as functions of zinc oxide content at constant TETD concentration. (2):  $k_{TD}^I$  and  $k_{DC}^I$  as functions of zinc oxide content with increasing amounts of a "constant ratio" mixture of [ZnO] and [TETD]. (3):  $k_{TD}^I$  and  $k_{DC}^I$  as functions of TETD concentration at constant zinc oxide content.

TETD decrease (Figure 3, right) and ZnDEDC increase (Figure 3, left) still comply with first order kinetics. The greater the amount of zinc oxide-TETD mixture (ratio = 12.5) added to the vulcanization mixture, the steeper are the lines representing ZnDEDC formation; i.e., the velocity constant of ZnDEDC formation becomes accordingly greater. On the other hand, the lines representing TETD decrease are practically parallel; i.e., the velocity constant of TETD decrease does not change under these conditions.

From the analytical data for TETD and ZnDEDC plotted in Figure 3 one can calculate the velocity constants  $k_{TD}^I$  and  $k_{DC}^I$  (see Table VII, No. 9-14). Plotting these constants against zinc oxide content one obtains a linear rise for  $k_{DC}^I$  and a line parallel to the abscissa for  $k_{TD}^I$ . Under these conditions  $k_{TD}^I$  is considered constant. Particularly it appears that the Curves II in Figure 2(1)

and 2(2) (similar scales for the abscissa) are parallel to one another. From this one concludes that the velocity constant of ZnDEDC formation is dependent upon the zinc oxide content and independent of TETD concentration. On the other hand, it appears that the velocity constant of TETD decrease responds to the  $[ZnO]:[TETD]$  mixing ratio. Therefore, Equation (2) for the variation of velocity constants of ZnDEDC formation retains its validity and the constant  $b$  in Equation (4) is independent of TETD concentration.

What happens when one uses a mixture with a constant zinc oxide content (250 millimoles in 100 g mixture) while successively increasing the TETD concentration is presented graphically in Figure 4. It shows that the velocity constant of ZnDEDC formation remains the same, since the curves in Figure 4, left, are practically parallel lines<sup>8</sup>. That is logical because, as emphasized al-

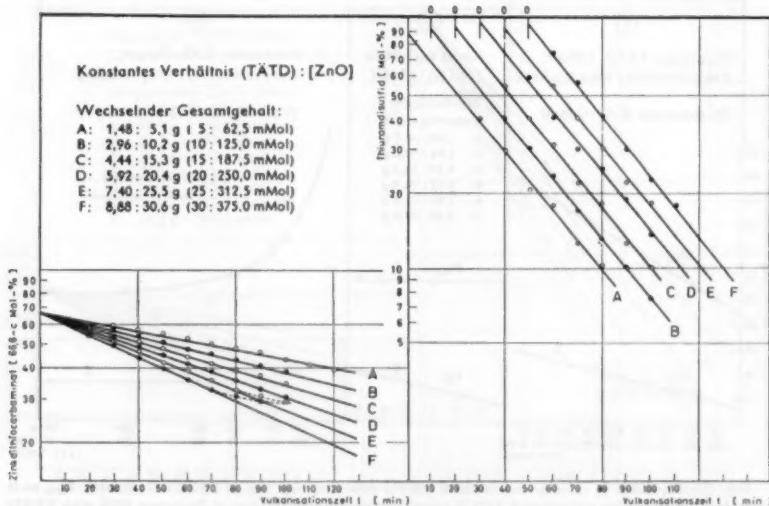


FIG. 3.—Progress of TETD decrease and ZnDEDC increase according to first order kinetics in vulcanization of Perbunan 2818 with TETD: increasing amounts of a "constant ratio" mixture of  $[ZnO]$  and  $[TETD]$ . Vulcanization temperature  $120^\circ C$ .

ready, the velocity constant of ZnDEDC formation depends upon the zinc oxide content which is held constant in this study. In comparison, the velocity constants of TETD decrease decline in the series of curves A through F (Figure 4, right) as shown by the changing slopes of lines A through F. With constant zinc oxide addition the velocity constants of TETD decrease decline with increasing concentration of TETD. That is also understandable since the velocity constant of TETD decrease depends upon the molar ratio  $[ZnO]:[TETD]$  which itself varies continuously in this study and becomes smaller in the series A to F.

In Figure 2(3) the velocity constants  $k_{TETD}^I$  and  $k_{BC}^I$  are plotted against the TETD concentration (millimoles or g in 100 g of mixture) (see the values in Table VII, No. 15-20). While the velocity constant of ZnDEDC formation follows a line parallel to the abscissa ( $k_{BC}^I = \text{constant}$ ), the velocity constant of

TETD decrease diminishes along the leg of a hyperbola and approaches a limit, namely  $\%k_{TD}^I$ .

The results described, which are all obtained for the vulcanization of Perbunan 2818 at 120°C, are likely to appear basic at other temperatures also. The reason for this will be given later since closer investigation of the temperature dependence of the relationship has required an extraordinary amount of work. Finally, no reason exists for the assumption that other tetraalkylthiuram disulfides should yield something other than those for TETD.

That the same results are obtained by work with natural rubber is illustrated by Figure 5 which shows that with constant concentration of TETD, but increasing additions of zinc oxide, the velocity constants of TETD decrease and of ZnDEDC increase both rise (Curves I and II). Figure 5 shows also that by

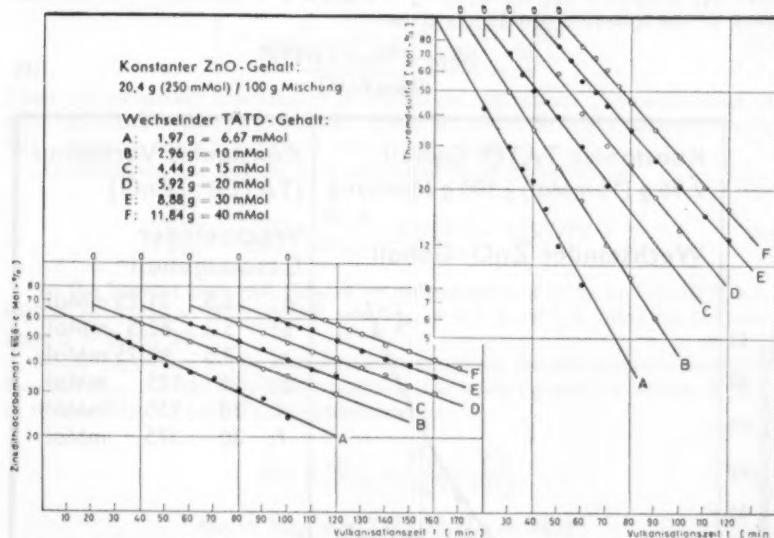


FIG. 4.—Progress of TETD decrease and of ZnDEDC increase according to first order kinetics in vulcanization of Perbunan 2818 with TETD; constant zinc oxide content, increasing TETD concentration A to F. Vulcanization temperature 120°C.

successive additions of a mixture of TETD and zinc oxide of the same molar ratio, the velocity constant of TETD decreases does not vary (Curve III) while that of ZnDEDC formation increases (Curve IV). Indeed Curves II and IV practically coincide, which is as it should be<sup>9</sup>. In principle the same situation holds for TETD vulcanization of natural rubber as for the corresponding experiments with Perbunan 2818. However, Curves I, II, and IV of Figure 5 display slight curvatures which is not the case in similar curves in Figure 2. It is possible that the high accuracy of measurement with Perbunan, as revealed in Figures 1-4, is traceable to the fact that Perbunan displays practically no degradation during milling; therefore, one always works with a starting material which remains the same in the final compound. This is not assured with natural rubber; and since it is very difficult for compounds having such different

amounts of zinc oxide and TETD in natural rubber to keep the milling times constant, one should expect a difference in the amount of degradation of rubber in different compounds. It is possible that the degree of curvature of the curves in Figure 5 can be taken as a measurement of the scattering of points.

Based on the results found in formulating the equations, it is pointed out, for a given Perbunan of constant average degree of polymerization that, thirum vulcanization can always be calculated.

In view of the relationships exhibited in Figure 2, one can express the velocity constant,  $k_{TD}^I$ , for the molar ratio  $[ZnO]:[TETD]$  as follows

$$k_{TD}^I = {}^0k_{TD} + {}^0k_{TD}^I a' \frac{[ZnO]}{[TETD]} \quad (5)$$

Here  ${}^0k_{TD}^I$  is equal to  $k_{TD}^I$  when  $[ZnO] = 0$  and  $a'$  is a constant. For the constant,  $a'$ , the following equation is given.

$$a' = \frac{(k_{TD}^I - {}^0k_{TD}^I)[TETD]}{{}^0k_{TD}^I [ZnO]} \quad (6)$$

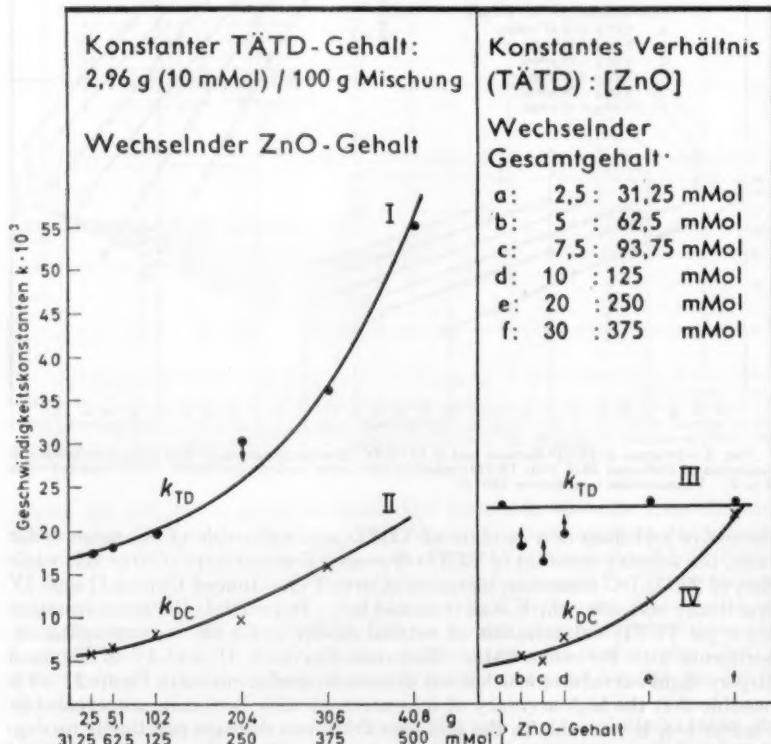


FIG. 5.—Variation of velocity constants of TETD decrease,  $k_{TD}^I$ , and of ZnDEDC increase,  $k_{DC}$ , as it depends upon zinc oxide content and TETD concentration in vulcanization of natural rubber with TETD at 120°C. Curves I and II: Dependence of  $k_{TD}^I$  and  $k_{DC}$  upon zinc oxide content at constant TETD concentration. Curves III and IV: Dependence of  $k_{TD}^I$  and  $k_{DC}$  upon zinc oxide content with increasing amounts of a "constant ratio" mixture of  $[ZnO]$  and  $[TETD]$ .

From the data in Column 6, Table VII, good uniformity is found for the values of  $a'$  calculated from Equation (6) for Perbunan 2818 on vulcanization with TETD at 120° C. A mean value of  $a' = 21.2 \times 10^{-3}$  is found. Equation (5) expresses that the velocity constant,  $k_{TD}^I$ , is a hyperbolic function of the TETD concentration at constant zinc oxide content, and particularly one obtains  $k_{TD}^I = {}^0k_{TD}^I$  when  $[TETD] \rightarrow \infty$ , shown also in Curve I in Figure 2(3).

By combining Equations (3) and (6) one obtains

$$a' = a[TETD] \quad \text{and} \quad a = \frac{a'}{[TETD]} \quad (7)$$

Division of Equation (3) by Equation (4) and substitution for the constant,  $a$ , according to Equation (7) gives

$$\frac{a}{b} = \frac{a'}{b[TETD]} = \frac{{}^0k_{DC}^I(k_{TD}^I - {}^0k_{TD}^I)}{{}^0k_{TD}^I(k_{DC}^I - {}^0k_{DC}^I)} \quad (8)$$

Thus,  $b$  is a constant independent of TETD concentration. The uniformity of  $b$  for the entire series of experiments comes out in the data of Column 7, Table VII. A mean value  $b = 6.03 \times 10^{-3}$  is calculated.

Furthermore, one obtains by transformation of Equation (8)

$$\frac{k_{DC}^I - {}^0k_{DC}^I}{k_{TD}^I - {}^0k_{TD}^I} = \frac{{}^0k_{DC}^I b}{{}^0k_{TD}^I a'} [TETD] = \alpha[TETD] \quad (9)$$

In the present case one obtains by substitution of  $a' = 21.1 \times 10^{-3}$ ,  $b = 6.03 \times 10^{-3}$ ,  ${}^0k_{TD}^I = 22.2 \times 10^{-3}$ , and  ${}^0k_{DC}^I = 3.2 \times 10^{-3}$ , a value for the constant  $\alpha = 4.1 \times 10^{-2}$ .

From Equation (9), related expressions appear for the velocity constants  $k_{TD}^I$  and  $k_{DC}^I$ . These should be valid with the known  $\alpha$  and the values of  ${}^0k_{TD}^I$  as well as  ${}^0k_{DC}^I$  for each TETD vulcanization.

$$k_{TD}^I = {}^0k_{DC}^I + \frac{k_{DC}^I - {}^0k_{DC}^I}{\alpha[TETD]} \quad (10)$$

$$k_{DC}^I = {}^0k_{DC}^I + \alpha[TETD](k_{TD}^I - {}^0k_{TD}^I) \quad (11)$$

Specifically, Equation (5) to (11) express what we have noted repeatedly in previous publications, namely that the TETD decrease and the ZnDEDC increase processes are related reactions. It is clearly apparent that vulcanization starts with the TETD decrease which takes place in contact with zinc oxide. Therefore, one must also assume that the recently discussed intermediate compound is formed with zinc oxide.

The preceding formal calculations and equations show that the kinetics of TETD vulcanization conform to certain laws which are related to the constituent concentrations and are fulfilled exactly by Perbunan. With the knowns  $\alpha$ ,  ${}^0k_{TD}^I$ , and  ${}^0k_{DC}^I$ , Equations (10) and (11) permit the calculation of velocity constants of ZnDEDC formation from velocity constants of TETD decrease at a given TETD concentration, and conversely. However, if one has once measured exactly the relationships corresponding to Figures 2(1) and 2(2) whereby it is sufficient to determine for the individual curves only a single point absolutely, then the velocity constants  $k_{TD}^I$  and  $k_{DC}^I$  can be calculated for any mixture whatever. It is seen that it is fundamentally possible to treat the

entire TETD vulcanization of a given Perbunan mathematically, which allows the tentative assumption that it is possible also in other cases.

In a previous paper<sup>10</sup> it was shown that, in TETD vulcanization of natural rubber, ZnDEDC formation and the crosslink reaction measured by the reciprocal swelling index are similar rate processes. Therefore, in practice, the ZnDEDC formation and the reciprocal swelling index are the more important results of TETD vulcanization. Even though no knowledge exists of the kinetics of the crosslink reaction with Perbunan, there is no reason for the assumption that the relationships between crosslinking and ZnDEDC formation found for natural rubber should not also be valid for Perbunan<sup>11</sup>. In any case, one may assume that the velocity constants of crosslinking can be calculated from the same Equation (2) as the ZnDEDC formation, so that in practice one can confine himself to the kinetics of the reciprocal swelling index. However, it is recommended that one find the functional dependence of the limiting value of the swelling index upon the TETD concentration, from which one can make definite statements about the degree of crosslinking.

These considerations seem noteworthy for practical use since one can calculate from the velocity constants the times, expressed in hours, within which the reaction reaches a degree of completion [50%, 75%, and the like]; i.e., it must also be possible to figure out curing times from knowledge of the velocity constants. For example, one can calculate from the velocity constants of the reciprocal swelling index, the curing time which must be used to obtain 75% or 50% of the possible crosslinking, etc. Corresponding considerations are naturally also possible with natural rubber. If care is taken to hold the degree of breakdown of the rubber constant, the curing time necessary to attain a determined degree of crosslinking should be calculable in the same way.

Of particular importance will be investigations the aim of which is to derive the relations between the kinetics of TETD vulcanization as shown by chemical reactions and conventional tension values obtained at the same time. It would be appropriate to draw on the kinetics of swelling to relate the chemical reaction and the physical property. Such investigations will be taken up on a broader basis in our institute.

#### SUMMARY

The present paper is concerned with the influence of TETD concentration and of zinc oxide content upon the kinetics of the vulcanization of natural rubber and Perbunan 2818 with TETD. The following results were obtained for vulcanization at 120° C.

1. The velocity constants of TETD decrease and ZnDEDC formation are linear functions of the zinc oxide content at constant TETD concentrations.
2. If TETD and zinc oxide are present in constant molar mixing ratios, then the velocity constant of TETD decrease is independent of the amount of the mixture while that of ZnDEDC formation rises linearly with zinc oxide addition.
3. The velocity constant of TETD decrease diminishes with increasing TETD concentration when the zinc oxide content of the mixture is held constant. Under these conditions the velocity constant of ZnDEDC formation remains unchanged.
4. Everything shows that the velocity constant of ZnDEDC formation depends only on the zinc oxide content of the mixture while that of TETD decrease is dependent on the molar ratio of zinc oxide and TETD.

5. The relationships found are expressed mathematically, and the practical significance of the relationships is pointed out.

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- <sup>3</sup> Scheele, W., and Stange, P., *Kautschuk und Gummi* 9, WT110 (1956).
- <sup>4</sup> Scheele, W., Lorenz, O., and Dünner, W., *Kautschuk und Gummi* 7, WT273 (1954); *ibid.* 8, WT2 (1955). See also Scheele, W., and Ilshner-Gensch, C., *Kautschuk und Gummi* 6, WT147 (1953), as well as Scheele, W., and Lorenz, O., *Kautschuk und Gummi* 9, WT27 (1956); Walter Scheele and coworkers, *RUBBER CHEM. & TECHNOL.* 29, 1 (1956).
- <sup>5</sup> That was found specifically in experiments with natural rubber; see also Scheele, W., and Stange, P., *Kautschuk und Gummi* 9, WT110 (1956). The ratios are for Perbunan only and therefore will not be tested again.
- <sup>6</sup> When no zinc oxide is present in the rubber mixture, TETD vulcanization proceeds differently so far as one can tell from a single vulcanization. That has been shown by D. Craig and coworkers and fully explained.
- <sup>7</sup> One observes that the curves in Figure 3, right are displaced along the abscissa (vulcanization time) a fixed amount since otherwise they would be superimposed.
- <sup>8</sup> Notice that in Figure 4 the curves are displaced along the abscissa also; otherwise the point of the curves would coincide. Curve A shows a somewhat greater slope; however, in view of the orderly location of the remaining curves, no particular significance is attributed to this deviation.
- Curve IV in Figure 5 shows a situation to which we have referred previously, that in TETD vulcanization of natural rubber, TETD decrease and ZnDEDG increase can become of the same velocity under special conditions. One sees that Curve IV at the highest zinc oxide content reaches Curve III. With still greater additions of zinc oxide perhaps it would rise no further.
- <sup>10</sup> Lorenz, O., Scheele, W., and Redetaky, W., *Kautschuk und Gummi* 9, WT269 (1956).
- <sup>11</sup> It is true that one must consider that Perbunan at higher temperatures thermovulcanizes, so that one must bear in mind in measuring the swelling index of a Perbunan cure that the constituent of thermovulcanization enters into the results of measurement. That this can be eliminated so that the variation of swelling produced in the vulcanization reaction will be measurable, will be shown shortly by O. Lorenz and H. Stemmer.

VULCANIZATION OF ELASTOMERS. 18.  
VULCANIZATION OF NATURAL RUBBER  
WITH SULFUR IN THE PRESENCE  
OF MERCAPTOBENZOTHIAZOLE. III \*

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INTRODUCTION

The kinetics of the sulfur vulcanization accelerated by mercaptobenzothiazole have been described in two previous publications<sup>1,2</sup>. It was shown, among other things, that both the decrease in the concentration of sulfur and the change of the reciprocal equilibrium swelling with time of vulcanization obey a first order rate law. These two processes occur at the same rate if the mixture (compounded stock) contains mercaptobenzothiazole or its zinc salt along with the sulfur and zinc oxide. If, however, zinc stearate is added to the mixture, the change with time of the reciprocal equilibrium swelling, which provides a measure of the crosslinking reaction, proceeds faster than the decrease in the sulfur. Moreover, the activation energies of the two processes are greatly reduced by the addition of zinc stearate. The decrease in the mercaptobenzothiazole concentration is temperature dependent in the absence of zinc stearate but not in its presence. The decrease in mercaptobenzothiazole follows a first order law in the presence of zinc stearate and has approximately the same rate as the decrease in sulfur.

In a vulcanization involving only sulfur, zinc oxide and mercaptobenzothiazole obviously only a few crosslinks are formed, since the products obtained exhibit very slight elasticity. This may be seen also in the comparatively high degree of swelling of the vulcanizate. Since the physical properties of the vulcanizates can be markedly improved by addition of zinc stearate, it appeared desirable to investigate in a quantitative manner the influence of the individual compounding ingredients (mercaptobenzothiazole, zinc stearate, sulfur and zinc oxide) on the decrease in the concentration of the sulfur as well as the mercaptobenzothiazole and the change with time of the reciprocal equilibrium swelling.

The influence of the mercaptobenzothiazole and zinc stearate (constant concentration of sulfur) on the kinetics of this vulcanization has already been described<sup>2</sup>. An important result of these studies was that the velocity constants for the sulfur decrease and the reciprocal equilibrium swelling, for a constant amount of zinc stearate, increase up to a mercaptobenzothiazole-zinc stearate molar ratio of about 4:1. Addition of mercaptobenzothiazole over and above this molar ratio causes no further rise in the velocity constants. Yet, if the stearate content is increased further, then increasing additions of mercaptobenzothiazole cause a renewed increase in the velocity constants until such

\* Translated by M. A. Golub for RUBBER CHEMISTRY AND TECHNOLOGY from *Kautschuk und Gummi 10*, WT273-277, November 1957.

time as the mixture again corresponds to a molar ratio of 4:1. Through the additions of mercaptobenzothiazole and zinc stearate in the molar ratio of 4:1 maximum accelerations of vulcanization are often obtained. This is clearly true for all vulcanization temperatures as was seen in the previous experiments, similar to those considered here.

We have concluded from these results that the acceleration of vulcanization involves an interaction of zinc stearate and mercaptobenzothiazole or its zinc salt, without, of course, being able to state exactly just how this may be demonstrated.

An examination of the results obtained with respect to the various functional relationships had shown that:

1. The velocity constant of the sulfur decrease, which is a first order process, is a linear function of the mercaptobenzothiazole content.
2. The velocity constant of the varying reciprocal equilibrium swelling, which likewise follows a first order reaction, increases linearly with the square root of the mercaptobenzothiazole content.

This is valid, however, only so long as the mercaptobenzothiazole-zinc stearate molar ratio is smaller than 4.

The investigations had also provided an insight into the degree of crosslinking attained at times, for which the limiting reciprocal equilibrium swelling is a suitable measure. It could be further shown that the amount of mercaptobenzothiazole does not influence the degree of crosslinking. However, the action of the zinc stearate is always tied in with the presence of the mercaptobenzothiazole according to a linear function of the square root of the stearate content.

The present paper deals with the influence of the concentration of sulfur and the zinc oxide content on the kinetics of vulcanization.

## RESULTS AND DISCUSSION

### THE MERCAPTOBENZOTHIAZOLE-ACCELERATED VULCANIZATION WITH VARIATION IN INITIAL SULFUR CONCENTRATION

The experiments were all carried out with mixtures containing 2.11 g of mercaptobenzothiazole, 2.00 g of zinc stearate (molar ratio, 4:1) and 4.07 g of zinc oxide with varying concentrations of sulfur. The vulcanization temperature was 120° C in all cases. The analytical results (uncombined sulfur as well as unconsumed accelerator in per cent and the reciprocal equilibrium swelling,  $1/Q_t$ ) are given in Table I, while the calculated velocity constants are presented in Table II. Since zinc benzothiazolylmercaptide is very rapidly formed from mercaptobenzothiazole and zinc oxide during vulcanization, the sum of mercaptobenzothiazole and its zinc salt was determined. The values calculated for this sum are given in Table I. The degree of swelling,  $Q_t$ , is expressed in terms of the amount of absorbed solvent (benzene) in grams per gram of vulcanizate.

At all initial concentrations of sulfur the decrease in sulfur is a first order reaction, so that plotting the logarithm of the uncombined sulfur against the time of vulcanization gives a straight line (Figure 1). The slope of the curves is bigger the smaller the initial concentration of sulfur. Although considerable effort was made to insure uniform conditions of mastication and mixing of ingredients in all the runs, induction periods decreased with increasing initial

concentration of sulfur and finally became negative (prevulcanization), as may be seen from Figure 1. The calculated velocity constants,  $k_s^I$ , were then plotted against the initial concentration of sulfur,  $[S]_0$ , as in Figure 2, from which it is seen that  $k_s^I$  approaches a limiting value corresponding to the velocity constant of the stearate-free vulcanization ( $0.15 \times 10^{-2} \text{ min}^{-1}$ ). Since a hyperbolic relationship is involved here, plotting  $k_s^I$  against the reciprocal of the initial sulfur concentration gives a straight line as seen in Figure 3. In the vulcanization of rubber (Perbunan 2818) with thiuram disulfide in the presence of zinc oxide<sup>3</sup> the velocity constant of the thiuram decrease is inversely proportional to the initial concentration of the thiuram disulfide. This analogy is noteworthy and it raises the question of whether, for other vulcanizing systems, similar relations

TABLE I  
EFFECT OF INITIAL SULFUR CONCENTRATION ON THE VULCANIZATION  
OF NATURAL RUBBER AT 120° C

Recipe:	Mercaptobenzothiazole	2.11 g (12.64 millimoles)					
Zinc stearate	2.00	(3.16 millimoles)					
Zinc oxide	4.07	(25.0 millimoles)					
Sulfur	Variable						
Pale crepe	Sufficient to make up 103 g of stock						
(A) 0.80 g (25 millimoles) Sulfur							
Vulc. time, min	20	25	30	40	50	60	∞
Uncombined S, %	43.1	28.2	20.2	8.4	3.6	1.8	
Unconsumed accelerator, %	95.6	94.7	93.8	92.9	92.4	92.0	91.9
$1/Q_t$ (Benzene)	0.076	0.101	0.116	0.131	0.138	0.137	0.141
(B) 1.60 g (50 millimoles) Sulfur							
Vulc. time, min	15	20	30	40	50	60	∞
Uncombined S, %	69.5	55.9	33.5	22.6	14.2	8.0	
Unconsumed accelerator, %	97.1	95.1	93.5	91.9	91.2	90.6	89.0
$1/Q_t$ (Benzene)	0.065	0.119	0.156	0.177	0.187	0.195	0.200
(C) 3.20 g (100 millimoles) Sulfur							
Vulc. time, min	15	20	30	40	60	80	∞
Uncombined S, %	81.7	72.8	58.1	46.0	30.6	19.8	
Unconsumed accelerator, %	96.8	94.5	92.4	89.4	85.8	84.4	81.0
$1/Q_t$ (Benzene)	0.049	0.104	0.176	0.209	0.239	0.253	0.260
(D) 4.80 g (150 millimoles) Sulfur							
Vulc. time, min	10	20	30	40	60	80	∞
Uncombined S, %	89.7	71.7	59.7	51.3	38.0	26.5	
Unconsumed accelerator, %	95.4	92.1	90.0	87.5	84.2	81.7	75.0
$1/Q_t$ (Benzene)	0.041	0.175	0.228	0.251	0.282	0.295	0.305
(E) 6.4 g (200 millimoles) Sulfur							
Vulc. time, min	10	20	30	40	60	80	∞
Uncombined S, %	89.4	72.3	65.4	53.8	41.3	34.1	
Unconsumed accelerator, %	—	—	—	—	—	—	
$1/Q_t$ (Benzene)	0.106	0.205	0.254	0.279	0.299	0.310	0.320
(F) 9.60 g (300 millimoles) Sulfur							
Vulc. time, min	15	30	45	60	80	100	∞
Uncombined S, %	80.0	67.4	59.7	55.3	46.2	41.8	
Unconsumed accelerator, %	92.9	85.4	81.5	77.6	75.9	72.6	53.0
$1/Q_t$ (Benzene)	0.189	0.283	0.320	0.341	0.359	0.371	0.380

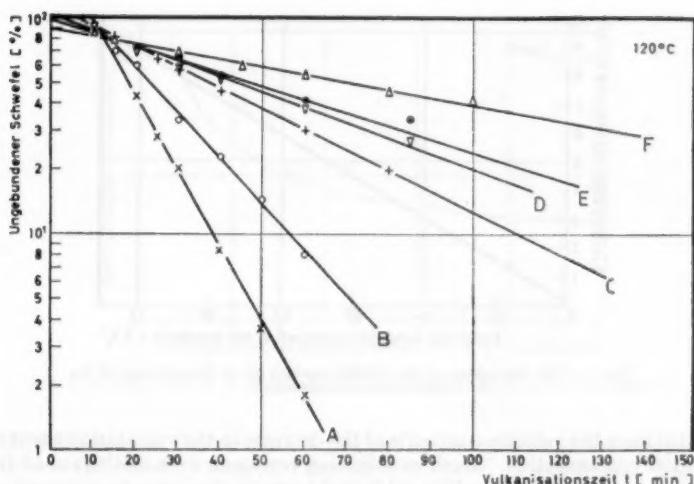


FIG. 1.—The first order decrease of sulfur for various initial concentrations of sulfur. See Table I for description of A to F.

TABLE II  
SUMMARY OF VELOCITY CONSTANTS FOR THE CURES OF TABLE I

Sulfur, g	$k_{\text{S}} \cdot 10^6$ (min <sup>-1</sup> )	$k_{\text{H}} \cdot 10^6$ (min <sup>-1</sup> )	$k_{\text{Q}} \cdot 10^6$ (min <sup>-1</sup> )
A	0.80	8.52	6.48
B	1.60	4.78	5.02
C	3.20	2.21	2.35
D	4.80	1.65	1.58
E	6.40	1.42	1.43
F	9.60	0.83	0.71

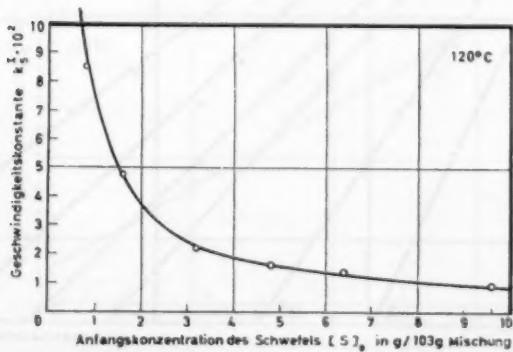


FIG. 2.—The dependence of the velocity constant  $k_{\text{S}}$  on the initial sulfur concentration.

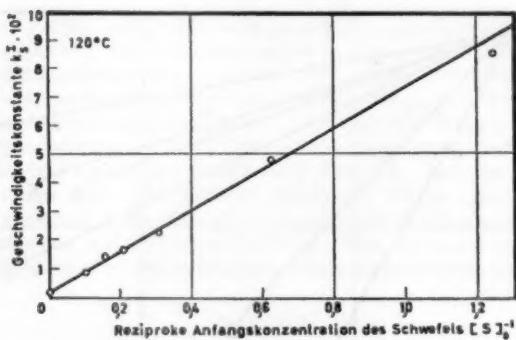


FIG. 3.—The dependence of the velocity constant  $k_s^1$  on the reciprocal of the initial sulfur concentration.

exist between the velocity constants of the decrease in the vulcanizing agent and its initial concentration. Such crosslinking reactions were distinguished from chemical reactions catalyzed by acids and bases in one important respect: for the latter reactions the velocity constant of the decrease in the reacting material is independent of its concentration and proportional only to the concentration of the catalyst.

After the detailed statement in the first section, it is understandable that, for the experiments under discussion here, the change with time of the reciprocal equilibrium swelling follows a first order law, as indicated in Figure 4. The curves in this figure are all displaced somewhat along the abscissa for purposes of clarity. The beginning of the heat-up period of the mixtures to bring them

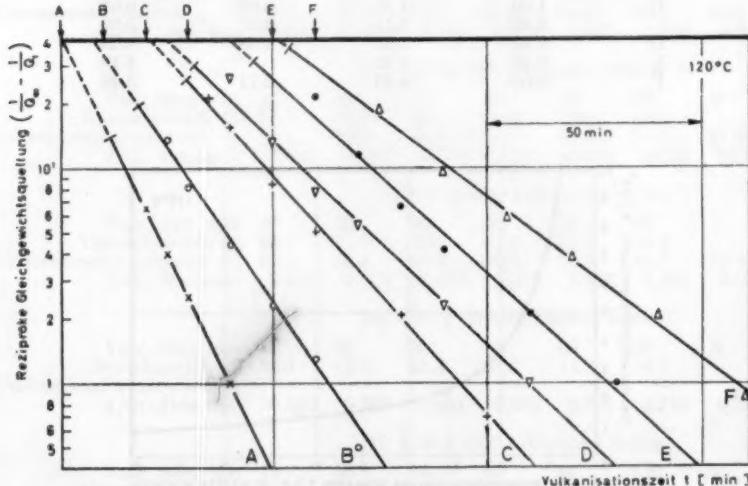


FIG. 4.—The first order change with time of the reciprocal equilibrium swelling for various initial sulfur concentrations.

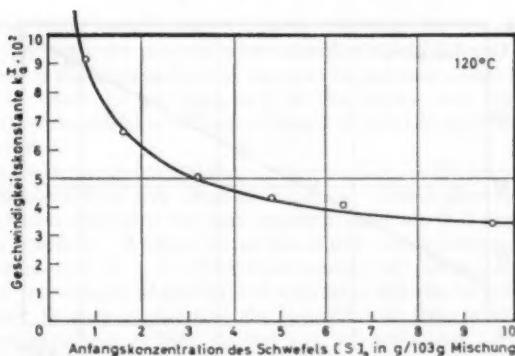


FIG. 5.—The dependence of the velocity constant  $k_q^I$  on the initial sulfur concentration.

to the vulcanization temperature is marked by an arrow, and the start of the reaction is indicated by a vertical line for each curve. Furthermore, it is seen that the induction periods become smaller and finally even negative with increasing sulfur content. A comparison with Figure 2 reveals that the crosslinking reaction and the sulfur decrease always set in at the same time. Figure 4 shows also that the velocity constants of the crosslinking reaction are smaller the higher the initial concentration of sulfur. This is seen even more clearly in Figure 5 where the calculated velocity constants are plotted against the initial concentration of sulfur,  $[S]_0$ . A curve is obtained similar to that for the dependence of the velocity constants of the sulfur decrease on the initial concentration of sulfur (see Figure 2). In this case  $k_q^I$  is proportional to the square root of the reciprocal initial concentration of sulfur. Figure 6 shows the straight line plot of  $k_q^I$  against  $[S]_0^{-1/2}$ . It was mentioned that the quotient  $k_q^I/k_s^I$  approaches the value of one at small initial concentrations of sulfur so that the crosslinking reaction and the sulfur decrease would then have the same rate. With increase in the amount of sulfur this quotient gets larger and at 10 weight per cent of sulfur, for example, has the value of 4. The swelling meas-

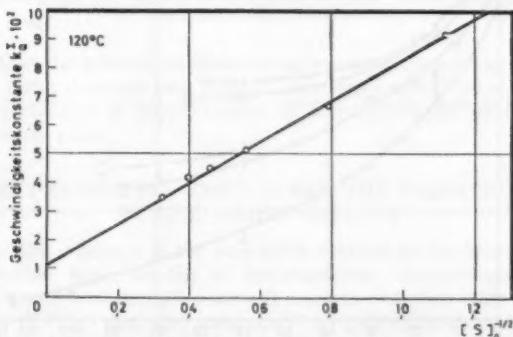


FIG. 6.—The dependence of the velocity constant  $k_q^I$  on the reciprocal of the square root of the initial sulfur concentration.

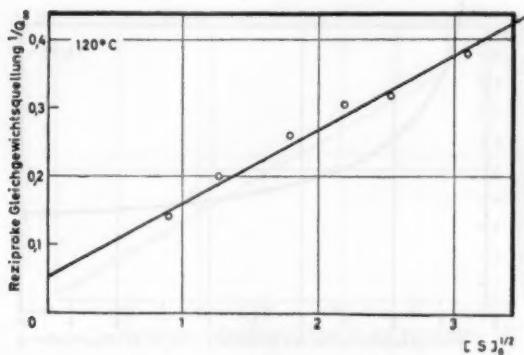


FIG. 7.—The dependence of the reciprocal equilibrium swelling on the square root of the initial sulfur concentration.

urements also provide data for the maximum number of crosslinks formed (given by  $1/Q_\infty$ ), which increases with increasing initial concentration of sulfur. An investigation of the functional relationship leads to the result that  $1/Q_\infty$  is proportional to the square root of the initial concentration of sulfur,  $[S]_0$ , as may be seen in Figure 7. The straight line does not cross the ordinate at the origin but rather at  $1/Q_\infty = 0.055$ . This is noteworthy since it indicates that a part of the crosslinking is not brought about by sulfur. This additional crosslinking is related to the presence of zinc stearate, and, as can be shown,  $1/Q_\infty$  is proportional to the square root of the stearate content<sup>2</sup>. We had previously noted that zinc stearate is not a vulcanizing agent; thus, no crosslinking occurs when rubber is heated with zinc stearate alone. Furthermore, it was observed that in vulcanization with sulfur in the presence of zinc oxide and zinc stearate the stearate had no influence on the degree of crosslinking. It is therefore clear that the increase in degree of crosslinking by zinc stearate in the presence of mercaptobenzothiazole can be explained on the basis of a selective reaction of sulfur with rubber, possibly tied in with the preferred creation of

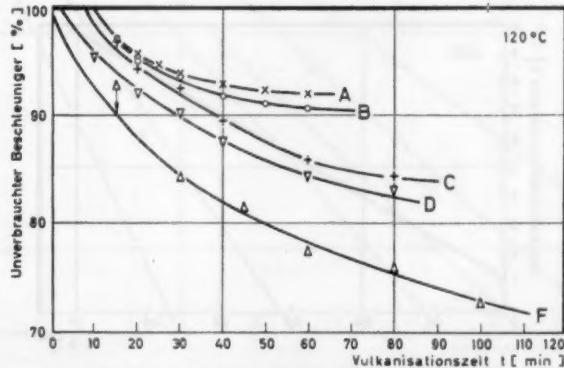


FIG. 8.—The decrease of the accelerator for various initial sulfur concentrations.

crosslinks of definite constitution. This is the case, for example, with the alteration of the ratio of intra- to intermolecular reaction between sulfur and rubber in favor of the intermolecular, but also in the case where the portion of the polysulfide bonds drops compared to the mono- and disulfide bonds. Further experiments will have to be performed in order to explain the action of the zinc stearate.

The decrease in the concentration of mercaptobenzothiazole as a function of the vulcanization time  $t$  is given in Figure 8. The higher the initial concentration of sulfur the more mercaptobenzothiazole which is consumed in the vulcanization reaction. A doubling of the sulfur concentration, for example, results approximately in a doubled consumption of mercaptobenzothiazole. The change of the amount of accelerator with time likewise follows a first order process, as may be seen by plotting the logarithm of the residual accelerator (maximum consumption = 100) against the vulcanization time (Figure 9).

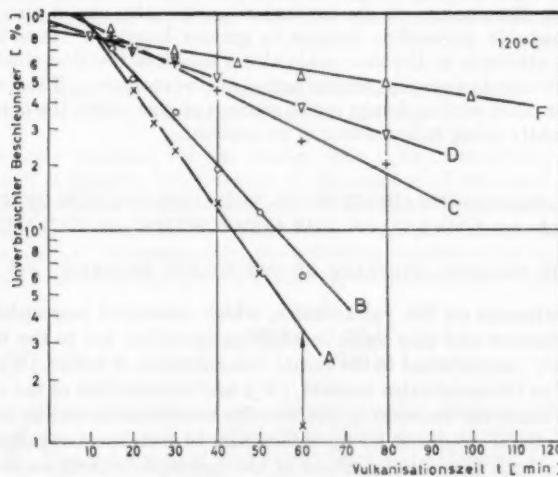


FIG. 9.—The first order decrease of the accelerator (maximum consumption = 100) for various initial sulfur concentrations.

It is notable that the velocity constants of accelerator decrease agree essentially with those of sulfur decrease (see Table II, columns 3 and 4); in other words, the corresponding changes in concentration of mercaptobenzothiazole and sulfur occur at the same rate.

#### EXPERIMENTAL RESULTS FOR THE VARIATION IN ZINC OXIDE CONTENT

A study of the influence of the zinc oxide content on the kinetics of vulcanization is another topic worthy of investigation. Accordingly, compounds weighing 103 g and containing a constant amount of sulfur (3.20 g), mercaptobenzothiazole (2.11 g) and zinc stearate (2.00 g) with increasing amounts of zinc oxide (2.04, 4.07, 8.14, 12.21 and 16.28 g) were vulcanized at 120° C. A consideration of the analytical results (not particularly presented here) showed

that the first order velocity constants of the sulfur decrease and the change with time of the reciprocal equilibrium swelling are essentially not influenced by a variation in the zinc oxide content. A small decrease of the constants with increasing amount of zinc oxide could be explained as a dilution effect. Also,  $1/Q_\infty$ , which is a measure of the maximum attainable degree of crosslinking, does not change with increasing amount of zinc oxide.

In the absence of zinc oxide entirely different conditions exist. Thus, not only is the velocity constant for sulfur decrease reduced, but in addition the maximum attainable degree of crosslinking becomes smaller. The calculated velocity constant,  $k_s^I$ , in the absence of zinc oxide in an otherwise identical compound it was  $1.16 \times 10^{-2} \text{ min}^{-1}$ , while in the presence of 4 weight per cent of zinc oxide in an otherwise identical compound it was  $2.21 \times 10^{-2} \text{ min}^{-1}$ . Moreover, the reciprocal equilibrium swelling displays a maximum over the time of vulcanization, i.e., it undergoes a reversion. Consequently, the determination of  $1/Q_\infty$ , obtained by means of an extrapolation of the function  $\log 1/Q_t = f(1/t)$  to  $1/t \rightarrow 0$ , is quite uncertain<sup>1</sup>. The reversion thus points to the formation, in the absence of zinc oxide, of thermally unstable polysulfide bridges in greater number<sup>4</sup>. It is necessary, therefore, to attribute to the zinc oxide also a selective reaction similar to the one already invoked to account for the action of zinc stearate. Thus, no change in  $1/Q_\infty$  takes place with a change in the amount of zinc oxide, the action of the latter apparently being independent of its amount.

#### EMPIRICAL EQUATIONS DESCRIBING THE DEPENDENCE OF THE CONSTANTS $k_s^I$ , $k_q^I$ AND $1/Q_\infty$ ON THE COMPOSITION OF THE MIXTURE

##### THE VELOCITY CONSTANT OF THE SULFUR DECREASE, $k_s^I$

The experiments on the vulcanizates, which contained mercaptobenzothiazole, zinc stearate and zinc oxide in addition to sulfur, led to the result that  $k_s^I$  is inversely proportional to the initial concentration of sulfur,  $[S]_0$ , directly proportional to the accelerator content,  $[B]_0$  and independent of the amount of zinc oxide. Since the increase in the velocity constants for sulfur decrease in the present case is produced by an interaction of mercaptobenzothiazole and zinc stearate, both the initial content of the mercaptobenzothiazole and that of the zinc stearate are contained in  $[B]_0$ . Since  $k_s^I$  at constant stearate content and increasing addition of mercaptobenzothiazole increases linearly until the mercaptobenzothiazole-zinc stearate molar ratio reaches 4:1, the particular concentration of the thiazole must always be inserted in  $[B]_0$  when the specified molar ratio is not exceeded. On the other hand, if the mixture contains even more mercaptobenzothiazole, that concentration must be inserted in  $[B]_0$  which corresponds exactly to that molar ratio. From a consideration of the velocity constants for stearate-free vulcanization the following expression is obtained for  $k_s^I$ :

$$k_s^I = {}^0k_s^I + \frac{a[B]_0}{b[S]_0} \quad (1)$$

${}^0k_s^I$  is the velocity constant for the sulfur decrease in a stearate-free vulcanization and  $a$  and  $b$  are constants which may be determined from the slopes of the linear functions  $k_s^I = f[B]_0$  (see Figure 9 of Paper XIII in this series) and  $k_s^I$

$= \varphi(1/[S]_0)$  (see Figure 3). Since sulfur decrease is a first order reaction in all the cases studied, it is also true that

$$k_{S^I} = {}^0k_{S^I} + \frac{a[B]_0}{b[S]_0} = \frac{1}{t} \ln \frac{[S]_0}{S} \quad (2)$$

The following differential equation is then obtained for the velocity of sulfur decrease,  $-\frac{d[S]}{dt}$ :

$$-\frac{d[S]}{dt} = {}^0k_{S^I}[S] + \frac{a[B]_0}{b[S]_0}[S] \quad (3)$$

In this equation the first term equals the reaction velocity in the absence of stearate, while the second term expresses the contribution to the reaction velocity of the acceleration resulting from the mercaptobenzothiazole and zinc stearate.

#### THE VELOCITY CONSTANT FOR THE RECIPROCAL EQUILIBRIUM SWELLING, $k_Q^I$

The velocity constant for the change with time of reciprocal equilibrium swelling,  $k_Q^I$ , is likewise independent of the amount of zinc oxide present, yet inversely proportional to the square root of the initial concentration of sulfur,  $[S]_0^{-\frac{1}{2}}$ , and proportional to the square root of the initial concentration of the accelerator,  $[B]_0^{\frac{1}{2}}$ . Consequently, the following expression for  $k_Q^I$  is obtained from a consideration of the velocity constants for stearate-free vulcanization:

$$k_Q^I = {}^0k_Q^I + \frac{a'[B]_0^{\frac{1}{2}}}{b'[S]_0^{\frac{1}{2}}} \quad (4)$$

Thus, for vulcanization without zinc stearate, sulfur decrease and the change with time of the reciprocal equilibrium swelling occur at the same rate, i.e.,  ${}^0k_{S^I} = {}^0k_Q^I$ . The constants  $a'$  and  $b'$  can likewise be determined graphically. As shown experimentally,  $b = b'$ , so that the two straight lines in Figures 3 and 6 have the same slope.

#### THE RECIPROCAL EQUILIBRIUM SWELLING, $1/Q_\infty$

The number of crosslinks formed—measured by the limiting value of reciprocal equilibrium swelling—is independent of the amount of mercaptobenzothiazole and zinc oxide. However, at constant initial concentration of sulfur it is proportional to the square root of the stearate content:

$$\frac{1}{Q_\infty} = \left( \frac{1}{Q_\infty} \right)_S + c[S]_0^{\frac{1}{2}} \quad (5)$$

$(1/Q_\infty)_S$  is the limiting value of the reciprocal equilibrium swelling in the absence of zinc stearate,  $c$  is a constant which can be calculated from the slope of the function  $1/Q_\infty = f[S]^{\frac{1}{2}}$ .

A similar equation is obtained for  $1/Q_\infty$  if the initial content of zinc stearate is held constant and the initial concentration of sulfur varied, namely,

$$\frac{1}{Q_\infty} = \left( \frac{1}{Q_\infty} \right)_{S_0} + d[S]_0^{\frac{1}{2}} \quad (6)$$

$(1/Q_\infty)_{S_0}$  represents the contribution to the over-all  $1/Q_\infty$  from the stearate and  $d$  is a constant which can also be determined graphically.

### SUMMARY

The present work is concerned with the influence of the concentration of sulfur and the zinc oxide content on the kinetics of the vulcanization of natural rubber with sulfur in the presence of mercaptobenzothiazole, zinc stearate and zinc oxide. The following results were obtained.

1. The velocity constant of the sulfur decrease,  $k_S^I$ , is inversely proportional to the initial concentration of sulfur.
2. The velocity constant of the change with time of the reciprocal equilibrium swelling,  $k_Q^I$ , is inversely proportional to the square root of the initial concentration of sulfur.
3. The limiting value of the reciprocal equilibrium swelling,  $1/Q_\infty$  (degree of crosslinking), at constant stearate content, is proportional to the square root of the initial concentration of sulfur.
4. The amount of accelerator consumed during vulcanization increases with increase in the initial amount of sulfur. The decrease in the accelerator is a first order reaction having approximately the same rate as the decrease of sulfur.
5. The velocity constants of the sulfur decrease and the change with time of the reciprocal equilibrium swelling are practically independent of the amount of zinc oxide. Other situations exist, of course, for compounds without zinc oxide.
6. Empirical equations were derived to express the dependence of the constants  $k_S^I$ ,  $k_Q^I$  and  $1/Q_\infty$  on the composition of the mixture.

### ACKNOWLEDGMENTS

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## EFFICIENCY OF TMTD VULCANIZATION \*

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Tetramethylthiuram disulfide (TMTD), together with a sufficient amount of zinc oxide, is the simplest and most efficient vulcanizing agent known for introduction of sulfur crosslinks into rubber<sup>1</sup>. No other combination approaches it in efficiency over a wide range of temperatures, although under limited conditions sulfur cures can be obtained with approximately as high a crosslink density per mole of vulcanizing agent<sup>2</sup>.

The stoichiometry of vulcanization with this curative has been explored in some detail in recent work of Scheele and coworkers<sup>3</sup>. They have confirmed the observation by Jarrijon<sup>4</sup> that during vulcanization dithiocarbamate is formed equivalent to close to two-thirds of the TMTD taken. The generality of this result was established in an exhaustive series of experiments, covering a range of structures of thiuram disulfide and of polyolefin, of temperature, and of concentration of reactants.

A tentative mechanism for the reaction of vulcanization with TMTD was outlined by Bielstein and Scheele<sup>5</sup>. In order to account for the high yield of dithiocarbamate, they adopted a suggestion advanced by Craig and coworkers<sup>6</sup> that a disulfide radical of the form:



is a key intermediate. The proposed mechanism predicts the observed ratio of dithiocarbamate formed during vulcanization to TMTD taken, and several other features of it appear to be subject to ready experimental test. Results obtained in this laboratory suggest that the mechanism of Bielstein and Scheele predicts accurately the stoichiometric relationships between the curative and sulfur in the vulcanizate and crosslinks formed, although there is some question as to details of the mechanism, which will be discussed separately.

This communication reports the results of a simple experiment designed to determine the ratio of firmly bound sulfur to crosslinks in an efficiently cured vulcanizate. Published estimates range from about one atom per crosslink to four<sup>7-9</sup>.

The careful work of Moore and Watson<sup>10</sup> has given evidence that di-*tert*-alkyl peroxides are probably nearly 100% efficient in the crosslinking of natural rubber. Assuming this to be true, we have compared the modulus of simple natural rubber compounds cured with cumyl peroxide and with TMTD. Since zinc oxide is required for cure with the latter compound, it was added to both series of samples to avoid masking of the modulus of the presence of filler. Both sets of compounds were cured in a platen press to full development of

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modulus at a nominal temperature of 150°, as determined by steam pressure. The results are shown in Table I and Figures 1 and 2.

In Table I, amounts of the two curatives (in moles/10<sup>4</sup> grams) which give

TABLE I  
EQUIVALENCE OF CURATIVES\*

Cumyl peroxide	TMTD
0.37	0.98
0.55	1.60
0.68	2.20
0.85	2.77
1.00	3.35
1.43	5.00

\* See text for explanation.

equal stress at 100 per cent elongation are given. These figures are interpolated from plots of experimental measurements of modulus as a function of curative concentration. The slope of the curve of TMTD as a function of cumyl peroxide, plotted from Table I, is 3.8.

Figure 1 contains data on combined sulfur and zinc dithiocarbamate formed

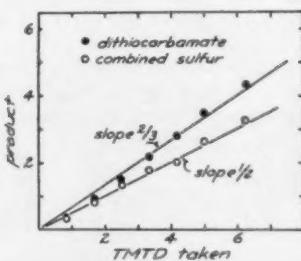


FIG. 1.—“Combined” sulfur and zinc dithiocarbamate formed during vulcanization of natural rubber as a function of TMTD used for cure. Units are moles (gram atoms of sulfur) per 10<sup>4</sup> grams rubber.

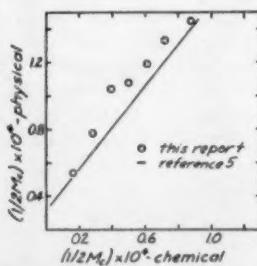


FIG. 2.—Comparison of “physical” crosslink density estimated from swelling measurements with “chemical” crosslinks assuming four moles of TMTD are required per crosslink formed.

during the vulcanization reaction. “Combined” sulfur was determined as total sulfur remaining in the stock after treatment with a mixture of hydrochloric and acetic acid followed by extraction with butanone. Dithiocarbamate was estimated by distilling carbon disulfide from a sample of the stock immersed in acidulated alcohol, which has been shown to be a quantitative procedure for recovery of dithiocarbamate in known mixtures. The disulfide was trapped in dimethylamine and its concentration estimated spectrophotometrically<sup>11</sup>.

In Figure 2 the crosslink density estimated from measurements of swelling of the sulfur cured vulcanizates in chloroform is plotted, in the form used by Moore and Watson, against crosslink density estimated from the data of Table I. The solid line in this figure is taken from the published figure<sup>10</sup>. The present results are considered to be in fairly good agreement with those of Moore and Watson, in view of the simplicity of the experimental procedure used here.

Combining the ratio of TMTD to crosslinks (four) obtained from Table I and the ratio of TMTD to firmly bound sulfur from Figure 1 (two), we obtain a maximum value for atoms for sulfur per crosslink of two. This does not establish that the sulfur is in fact in the crosslink.

The observed ratio of sulfur to crosslinks is consistent with the mechanism discussed by Bielstein and Scheele, but more TMTD was required than is called for in their scheme<sup>12,13</sup>. The excess requirement may be a measure of loss of the thiram disulfide in side reactions such as the one outlined by Craig<sup>6</sup>. This is currently under investigation.

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- <sup>13</sup> This is contribution No. 171 from the United States Rubber Company Research Center, Wayne, New Jersey.

## EQUIVALENT CURES IN SPECIMENS OF VARIOUS SHAPES \*

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The job of studying the problem of equivalent cures in rubber specimens of various shapes and thicknesses was assigned to a task group of subcommittee 10 of ASTM Committee D-11 in February, 1957. The assignment was not clear cut, and it was soon apparent that two separate and distinct phases were involved:

(1) How does one adjust the curing times for various shapes and thicknesses to accomplish the same state of cure as in a standard tensile sheet at some specified time and temperature?

(2) How does either the manufacturer or the consumer determine that he has equivalent states of cure when he has a standard tensile sheet cured at a specified time and temperature and a product of different size and shape, but cured at a different time and temperature?

A report presented here of the work of a task group of subcommittee 10 on physical testing of Committee D-11 on Rubber of the American Society for Testing Materials at its meeting in St. Louis, Mo., February 10-14, 1948 seems to provide answers to this problem.

### ADJUSTMENT OF CURE TIMES

A solution to the first phase of the problem requires a knowledge of the thermal properties of the stock in question, the dimensions of the part to be considered, and the temperature dependence of vulcanization. The latter information is also useful when it is required to transpose cures from one temperature to another.

The problem is confined to determining the added time required to adjust the cure for thicknesses greater than that of a standard tensile sheet. For articles of lesser thickness, no adjustment is required.

*Incubation time.*—The nomograph shown in Figure 1 permits the calculation of the lag time or incubation time for articles of varying shapes and of varying compositions. The most favorable shape for low lag time is a sphere; while the most unfavorable shape is a thick flat slab of relatively large width and length. The second factor is the minimum dimension. In the case of the sphere this is the diameter, and for a large flat slab it is the thickness. For a block one by two by three inches it would be the one-inch dimension.

\* Reprinted from *Rubber World*, Vol. 137, pages 856-859, March 1958.

The thermal diffusivity is important since this controls the rate of conductance of temperature through the object. The large effect of this factor can be seen at a glance.

It will be seen that the incubation time as scaled from this nomograph is assumed to be independent of the temperature, which is not strictly the case, since if the cure were to be conducted at room temperature, there would be no incubation time. As the impressed temperature increases, the incubation time increases. The nomograph can be assumed to be accurate at 280° F, with approximately a 5 per cent error for temperatures 60° F higher or lower than 280° F.

Once the incubation time is determined, it is simply added to the cure time of the tensile sheet provided the latter is greater than the former. If the incubation time is longer than the tensile sheet cure, however, a correction needs to be applied which is obtained from the curve in Figure 2. The ratio of the tensile

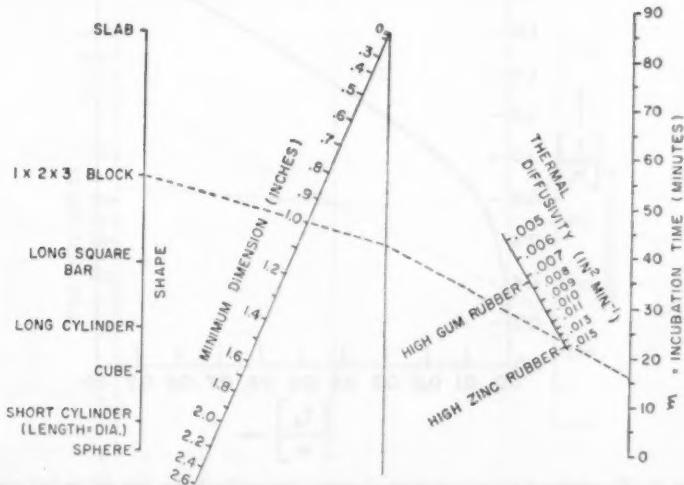


FIG. 1.—The size, shape, and compound composition of the article to be cured determine an "incubation" time. This time, denoted by  $m$ , may be obtained from the above nomograph. Intermediate shapes may be interpolated on the left-hand scale. The dotted line, for example, shows that a one- by two- by three-inch block of tread stock will have an incubation period of 16 minutes.

sheet cure,  $t_c$ , to the incubation time,  $m$ , is first calculated. Then from the curve the factor  $t/m$  is scaled. This latter factor multiplied by the incubation time gives the cure time.

Thus if the cure time for a tensile sheet is 12 minutes, and the incubation time is 120 minutes, the ratio of  $t_c/m = 0.10$ . From the curve,  $t/m = 0.87$ , whence  $t = 120 \times 0.87 = 104$  minutes.

The construction of both the nomograph and the curve in Figure 2 involves calculations of the curing effect obtained during the heating-up period at temperatures lower than the impressed temperatures. To do this requires an assumption as to the temperature dependence of the cure rate. For this calculation it was assumed that the cure rate is doubled for an 18° F increase in tem-

perature. There are differences of opinion as to the value of this factor and claims that different curing systems and different polymers respond somewhat differently.

A careful look at published data, however, suggests that most of the work was not too carefully done, and some results are based on sulfur combinations which are not applicable. The value used is an average figure which we believe to be fairly accurate. Actually a large error in this factor makes only a minor difference in the calculations; so this point is relatively unimportant.

*Temperature transposition.*—Since frequently the establishment of a cure for a product involves not only an estimate of the incubation time, but also a transposition from one curing temperature to another, it should be possible to transpose easily from one temperature to another. In this case the temperature co-

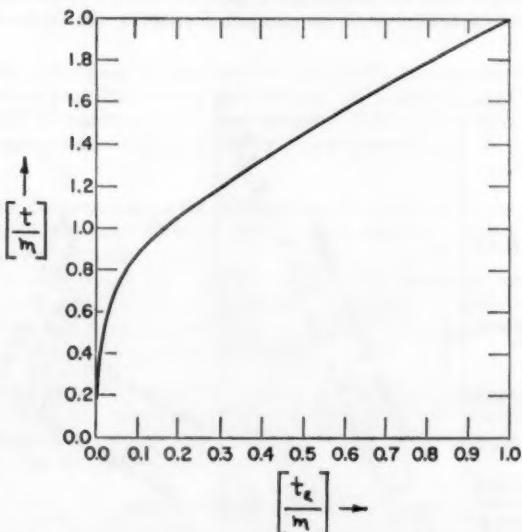


FIG. 2.—The relation of the ratios of tensile sheet cure time and incubation time and product cure time and incubation time is used to obtain a correction factor when the product incubation time, as obtained from Figure 1, is greater than the tensile sheet cure time.

efficient is more important. Most technical men have one or several charts which have been published or prepared in their own company. These are based on various values for the temperature coefficient, and most are subject to some question for the reasons given above.

The assumption that a factor such as 2/10° C will apply over the entire temperature scale is subject to an appreciable error for temperatures which are different by a considerable amount. The rate of cure should depend on the absolute temperature, and its logarithm should be inversely proportional to the reciprocal of the absolute temperature. The error is due to the fact that the differences between the reciprocals of curing temperatures which are 10° C apart are different at the low end of the range, e.g., 110° C-120° C from those at the high end of the range, e.g., 160° C-170° C.

The nomograph—Figure 3—was constructed on the basis of a reciprocal

temperature scale on the right. The latter was constructed on the basis that in the 280° F range the rate of cure is doubled for an 18° F increase in temperature.

One additional point should be mentioned. If it is desired to transpose the cure of an article from one temperature to another, and the cure time includes an incubation time, the latter should first be subtracted from the cure time before the temperature transposition is made.

The mistake which would result can be illustrated as follows:

Suppose a product is being cured 60 minutes at 280° F, and the tensile sheet cure is 40 minutes at 280°, and incubation time for the product cure is 20 minutes. If it is desired to cure this product at 300° F, and the 60-minutes-at-280° cure is transposed by Figure 3 to 300° F, we have 28 minutes at 300° F.

If the incubation time of 20 minutes, however, is first subtracted and the transposition made, we find that 40 minutes at 280° F is equal to 18 minutes at

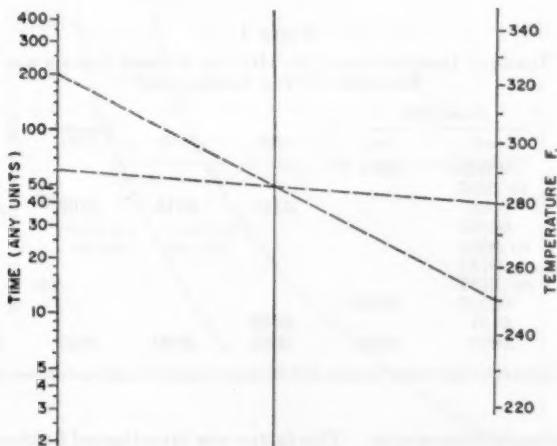


FIG. 3.—Nomograph for transposing cure time at one temperature to cure time at a different temperature.

300° F, and to this is added the 20-minute incubation time, giving a new cure of 38 minutes at a temperature of 300° F.

The reason for this modification of the procedure for equivalent cure determination is the point made earlier that the incubation time is essentially independent of the impressed temperature.

**Method check.**—In the operation of this equivalent cure procedure there are usually two estimates involved which can be in error. In estimating the shape factor the product being considered is usually not a simple geometric shape, and judgment or a guess is involved as to what point to select on the left-hand scale of Figure 1. The second estimate involves the thermal diffusivity of the stock in question, which is not usually known with any certainty. Several values are indicated on the scale as a guide. Also in Table I are listed some published data on certain rubbers and compositions.

In practice the usual procedure involves a calculation of the incubation time based on the best estimates of the shape factor and the thermal diffusivity. A trial cure is then run; and based on tests or observations, an adjustment may or may not be required.

As an illustration of a means by which the lag time or incubation time may be determined as a check against the nomograph of Figure 1, were prepared slabs  $\frac{1}{2}$ -inch thick and one inch thick and a series of cures run for several of the compositions given in ASTM Method D 15-55T, Method of Sample Preparation for Physical Testing of Rubber Products. Swelling tests were run on specimens cut from tensile sheets cured 40 minutes as well as specimens cut from each of the cures for the thicker slabs. A vertical slice approximately 0.075-inch thick was cut near the middle of each slab, and from these slices specimens were prepared for immersion tests.

Thus each specimen included the more highly cured top and bottom surfaces as well as the less highly cured center section. Swelling tests were run in three laboratories. The results obtained were somewhat erratic, particularly

TABLE I  
THERMAL DIFFUSIVITIES ( $\text{IN}^2/\text{MIN}$ ) OF RUBBER COMPOUNDS  
REPORTED IN THE LITERATURE\*

Reference	Hevea (NR)		SBR	NBR	Neoprene (CR)	Butyl (IIR)
	Tread	Gum				
(1)	.00613	.0064				
	to .0015					
(2)	.0102		.0115	.0115	.0102	.00836
(3)	.00465					
	to .0093					
(4)	.00743					
	to .0130					
(5)	.00912	.00938				
(6)	.0131		.0152			
(7)	.0094	.0062	.0063	.0080	.0067	.0053

\* NOTE: Thermal diffusivity values increase with increased pigment loading and decrease with increasing temperature.

with the natural rubber stocks. This factor was investigated further and found to be due to reversion of these stocks with continued cure which gave U-shaped curves of swell versus time of cure, which do not lend themselves well to this technique.

One set of results which came out reasonably well is illustrated in Figure 4. These results were obtained with a SBR tread-type stock, and the data plotted are the averages of the results from the three participating laboratories.

The lag time is scaled off and shown on the curve along with the lag times calculated from Figure 1, using 0.014 as the thermal diffusivity. The agreement is reasonably good.

#### PRODUCT VERSUS TENSILE SHEET CURE

For the second phase of the assignment a procedure is required by means of which the state of cure in a product can be compared with the state of cure in a tensile sheet given the "best" or most desirable cure.

The solution of this problem requires the selection of a property which is sensitive to state of cure. Further, the property should be capable of being

accurately measured on specimens of shapes and dimensions different from that of a tensile sheet. Some properties which might be considered are the following:

(1) Free Sulfur. This determination is applicable only to those materials which are vulcanized with elemental sulfur. It is a good method, when applicable, and does not depend on the geometry of the specimens.

(2) Solvent Swelling. This test is very sensitive to state of cure. It is applicable to articles or specimens of various shapes provided the material does

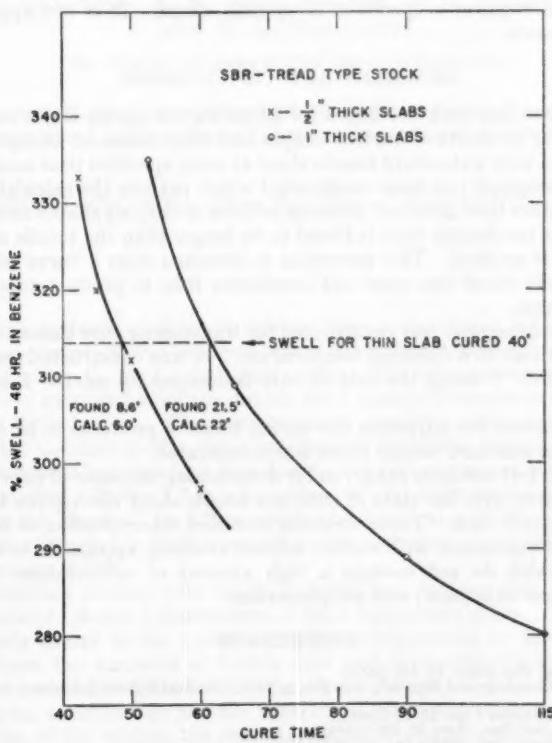


FIG. 4.—Cure times (calculated and found) for one-half and one-inch slabs of SBR tread-type stocks.

not contain a high proportion of extractables. If so, specimens of identical size and shape from both the tensile sheet and the product are necessary.

(3) Hardness. Hardness tests are fairly sensitive to state of cure, but also dependent on shape and size of specimen.

(4) Stress-Strain, Modulus at Low Extension, Ultimate Tensile and Elongation. Modulus and breaking elongation are very sensitive to state of cure and in some cases tensile strength also. All are influenced, however, by the geometry of the sample, and if buffing is required, both ultimate tensile and

elongation are affected. Of these properties, modulus at a low extension is probably the best choice for comparative cure tests.

(5) Set Properties. Compression set, tension set, creep, and stress-relaxation are all sensitive to state of cure. Compression set may be determined by plying up disks cut from tensile sheets, and if a standard specimen or disks which may be plied up to  $\frac{1}{2}$ -inch in thickness can be obtained from the article, a good comparison can be obtained. The usefulness of the other tests depends on the possibility of obtaining suitable test specimens.

(6) T-50 Test. This test is sensitive to state of cure for natural rubber products and requires a specimen of specific shape. It is not applicable to other elastomers.

#### SUMMARY AND CONCLUSIONS

A procedure has been developed for adjusting the curing times and state of cure of rubber products of various shapes and thicknesses to be equivalent to that obtained with a standard tensile sheet at some specified time and temperature. A nomograph has been constructed which permits the calculation of the lag or incubation time involved in curing articles of varying shapes and compositions. If the incubation time is found to be longer than the tensile sheet cure, a correction is applied. This correction is obtained from a curve relating the ratios of tensile sheet cure time and incubation time to product cure time and incubation time.

Another nomograph was constructed for transposing cure times at one temperature to those at a different temperature. It was constructed on the basis that in the 280° F range the rate of cure is doubled for an 18° F increase in temperature.

This procedure for adjusting the curing times of products to be equivalent to that of the standard tensile sheet is demonstrated.

Suggested test methods are given for determining the state of cure in a product as compared with the state of cure in a tensile sheet when given the "best" or most desirable cure. These methods included determination of free sulfur, for materials vulcanized with sulfur; solvent swelling, applicable to articles or specimens which do not contain a high amount of extractables; hardness; modulus at low extension; and set properties.

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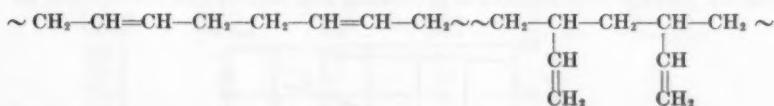
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# THE INFLUENCE OF STRUCTURE ON THE CHEMICAL ACTIVITY AND VULCANIZABILITY OF BUTADIENE POLYMERS \*

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In polymerization of butadiene and its derivatives, the monomer groups join in various positions. The 1,4- and 1,2-structures are most commonly indicated as follows:



The relative contents of these structures have a significant influence on the physical properties of the polymer (glass transition temperature, degree of orientation, strength, etc.). It is also evident that differences in the position and nature of substitution of the double bond cause differences in the chemical activity of the polymers. These differences in chemical activity are also determined by the fact that the 1,4-structure contains methylene groups in the  $\alpha$ -position to the double bonds, which therefore have hydrogen atoms with weakened bonds on carbon. In the 1,2-structure there is a hydrogen atom attached to a tertiary carbon atom. The differences in the chemical activities of butadiene polymers were studied in their interaction with perbenzoic acid, iodine chloride, and elementary sulfur.

The materials studied were synthetic butadiene rubbers with various relative contents of 1,4- and 1,2-structures in their molecular chains. The contents of vinyl side chains in the 1,2-structure were determined by the ozonization method, from the amounts of formic acid and formaldehyde split off<sup>1</sup>; the double bond contents of the 1,4-structure were determined from the difference between total unsaturation and the contents of vinyl side chains.

For some of the rubbers the results were confirmed by spectrographic data from the characteristic frequencies of  $965 \text{ cm}^{-1}$  for double bonds of the 1,4-structure and  $909 \text{ cm}^{-1}$  for monosubstituted double bonds of the 1,2 structure.

*Interaction with perbenzoic acid.*—The reaction of unsaturated compounds with perbenzoic acid was studied in detail by Prilezhaev<sup>2</sup>. He established that the rate of the perbenzoic acid reaction depends on the positions and nature of the substituents at the double bonds. The chief direction of the reaction is the formation of epoxide groups in the polymer, in amounts equivalent to the benzoic acid formed. Meyer has proposed the use of the Prilezhaev reaction for determination of the structure of butadiene polymers by calculating the content

\*Reprinted from *Colloid Journal (USSR)* 19, 199-206 (1957); translated by Consultants Bureau, Inc. from *Kolloidnii Zhurnal*, Vol. 19, pages 188-197 (1957).

of 1,4 structural units with the aid of a special diagram, based on the results of titration of model low-molecular hydrocarbons under the same conditions. Meyer's work, carried out in the laboratory of the Schkopau works, has not been published; it is mentioned by Weindlein<sup>3</sup>. The kinetic method for the determination of the structure of butadiene rubbers by the perbenzoic acid reaction was developed by Dogadkin and Dobromyslova<sup>4</sup>. Saffer and Johnson<sup>5</sup> consider that this method is applicable only to polymers containing more than 70% of internal double bonds. Our kinetic investigations showed that, in chlorobenzene medium with 0.1 N concentration of the rubber at 20°, both types of double bonds react with perbenzoic acid, but at very different rates. Figure 1 shows the kinetics of the reactions of benzoic acid with solutions of natural rubber, one of the butadiene polymers, and vinylcyclohexene as a model substance containing a disubstituted double bond in the ring and a mono-substituted double bond in the vinyl side chain. The amount of perbenzoic acid consumed was determined by titration with 0.1 N thiosulfate solution. Natural rubber, which contains only the 1,4-structure in its molecules, reacts rapidly, and the total amount of perbenzoic acid decomposed corresponds (to

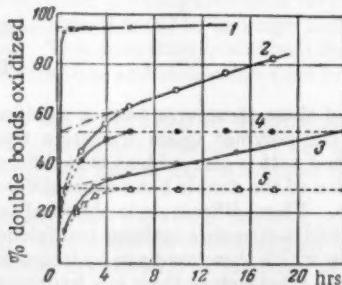


FIG. 1.—Kinetics of oxidation of vinylcyclohexene and different rubbers by perbenzoic acid: 1) natural rubber; 2) vinylcyclohexene; 3) butadiene polymer SR-1; 4,5) kinetics of double bond oxidation in the 1,4-structure of vinylcyclohexene and butadiene polymer SR-1.

within 2%) to  $\alpha$ , the total unsaturation of this compound (Curve 1). The kinetic curve for the oxidation of vinylcyclohexene contains two distinct regions—an initial region of steep ascent, and a final linear region which represents the reaction proceeding at a low constant rate. If the linear region is extrapolated to the ordinate axis, it cuts off an intercept corresponding to 50% of the total number of double bonds in vinylcyclohexene. From this it may be concluded that the linear region represents the oxidation kinetics of the less active vinyl groups, while the steeply ascending region corresponds to rapid oxidation of disubstituted double bonds in the ring. By drawing a horizontal straight line from the point of intersection of the linear region with the ordinate axis, it is possible to find ordinates corresponding to slow oxidation of vinyl groups, for each time instant on the experimental curve, and to plot a theoretical curve representing oxidation of the double bonds in the ring only (Curve 4).

The kinetic curves for the reaction of perbenzoic acid with butadiene polymers are of similar form, since the latter contain two kinds of double bonds in their chains (Figure 2). The double bonds in the vinyl side chains are oxidized very slowly, and therefore at a constant rate, because their concentration does not change significantly during the time of observation. By extrapolating the

linear regions of the kinetic curves to the ordinate axis, it is possible to determine the initial contents of double bonds of the 1,4-structure, and to plot the kinetic curve for the oxidation of the 1,4-structure (Figure 2, Curve 5) as described above.

The validity of this method of segregating the oxidation processes of different types of double bonds, and of their quantitative determination, is confirmed by data on ozonization of the same polymers (Figure 2 and Table I).

TABLE I  
CHARACTER OF BUTADIENE POLYMER DOUBLE BONDS

Type of rubber	Total unsaturation in %, by the CLI reaction	% content of structures		By difference between total unsaturation and contents of 1,4-structure	Sum of double bond contents of 1,4- and 1,2-structure by oxidation with perbenzoic acid and ozonation
		1,4	1,2		
SR-1	87	30	57	57	87
SR-2	92	49	40	43	89
SR-3	94	65	31	29	96
SR-4	94	30	—	64	—
SR-7	96	43	—	53	—
SR-5	95	50	—	45	—
SR-6	96	65	—	31	—

The values for the double bonds of different structures in seven grades of synthetic rubber, determined from kinetic data with perbenzoic acid, are in good agreement with the values obtained from ozonization data and data on the reaction with iodine chloride.

*Interaction with iodine chloride.*—Reactions of rubbers with halogens have been frequently studied. The reactions are complex in character, and vary according to conditions, both in their mechanism and in the intermediate steps

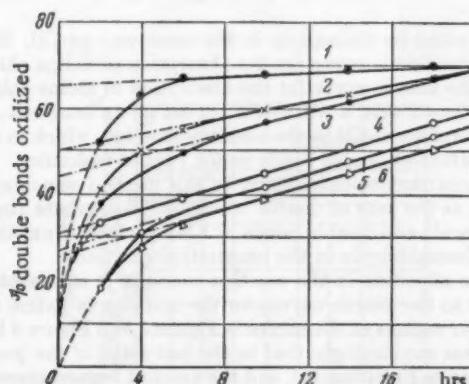
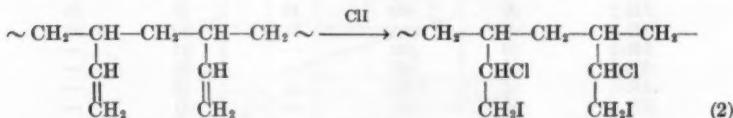
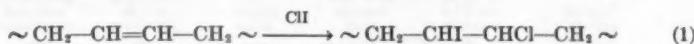


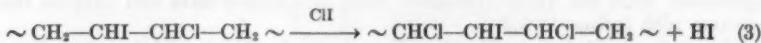
Fig. 2.—Kinetics of oxidation of various butadiene rubbers by perbenzoic acid:  
1) SR-6; 2) SR-5; 3) SR-7; 4) SR-4; 5) SR-8; 6) SR-9.

and final results. In many cases, addition of halogens at the double bonds is accompanied by substitution of hydrogen at the  $\alpha$ -methylene groups and formation of intramolecular rings<sup>6</sup>. The structure of the polymer has a significant effect on the course of the reaction. We studied the reaction between iodine chloride and butadiene polymers with various contents of 1,4- and 1,2-structures. The reaction was carried out by mixing 0.05 M (calculated on the unit molecular weight) of the rubber solution in dichloroethane with 0.2 N solution of iodine chloride in the same solvent. The halogen was in 100% excess above the theoretical amount. The course of the reaction was followed by the consumption of iodine chloride (by titration of samples with thiosulfate) and by formation of iodine (titration of samples with potassium iodate).

As Figure 3 shows, absorption of iodine chloride by the polymer at 20° proceeds at a high rate during the first 6–8 hours; subsequently the reaction slows down and continues for a long time at a low constant rate (linear region of the kinetic curve). The initial region mainly represents the addition of iodine chloride at the double bonds<sup>6</sup> according to the schemes:



The linear region represents the slow reaction of hydrogen substitution, which probably occurs according to the scheme:



As the result of the last reaction, an equivalent amount of iodine is liberated:



Since  $\text{I}_2$  is titrated by thiosulfate in the same way as ClI, Reaction (4) is not reflected in the kinetic curve for the absorption of iodine chloride. If the linear region of the kinetic curve for the absorption of iodine chloride is extrapolated to the ordinate axis, it will evidently cut off an intercept corresponding to maximum absorption of ClI in the addition reaction, which in its turn corresponds to the content of double bonds in the rubber molecules.

In fact, the unsaturation determined by this method coincides with the unsaturation found as the sum of double bonds of 1,4-structure (by the reaction with perbenzoic acid) and double bonds of 1,2-structure (from the amounts of formic acid and formaldehyde in the ozonization reaction).

The liberation of iodine in the reaction medium is represented by kinetic curves analogous to the kinetic curves for the addition of iodine chloride (Figure 4). The linear regions of the curves in Figure 3 and Figure 4 have the same slope. This proves convincingly that in the last stage of the process iodine is liberated according to Equation (4), and the amount formed corresponds to the HI split off in the substitution reaction represented by Equation (3). The initial rapid liberation of iodine is probably associated with a cyclization re-

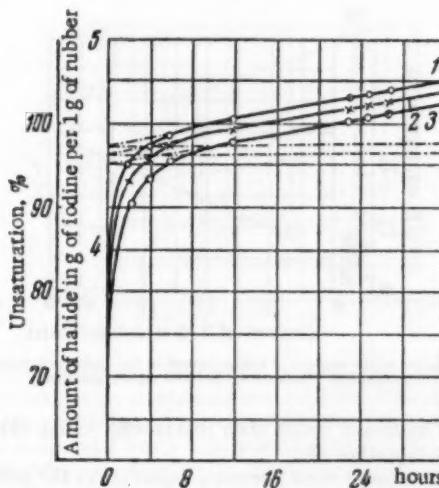


FIG. 3.—Kinetics of iodine chloride absorption in the reaction with butadiene polymers: 1) SR-4; 2) SR-5; 3) SR-6.

action\*. If the linear region of the kinetic curve for iodine liberation is extrapolated to the ordinate axis, the intercept cut off is a measure of the maximum amount of iodine liberated in cyclization. As Figure 5 shows, this amount increases linearly with increase of the content of the 1,2-structure in the molecules of the different rubbers. This suggests that cyclization occurs predominantly in the 1,2-structure according to the following scheme:

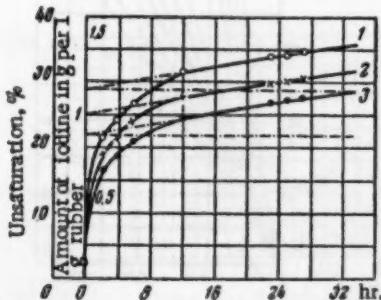
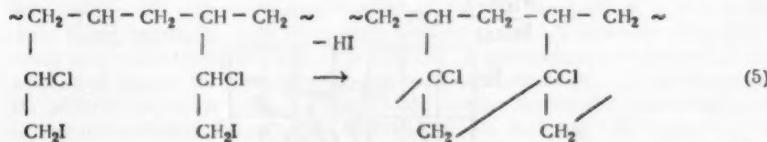


FIG. 4.—Kinetics of iodine formation in the reaction of iodine chloride with butadiene polymers: 1) SR-4; 2) SR-5; 3) SR-6.

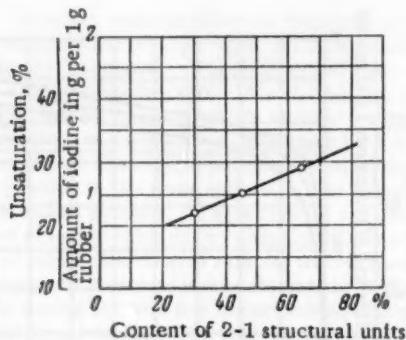


FIG. 5.—Variation of the amount of iodine formed in the cyclisation reaction with the contents of 1,2-structural units in various polymers.

The liberated hydrogen iodide then reacts with iodine chloride to form iodine according to Equation (4).

Thus, different rubbers show the same behavior in the addition reaction at the double bonds, in the reaction with iodine chloride under the conditions studied. The cyclization process, in the other hand, develops mainly in the structure with vinyl side chains; this may be attributed to steric conditions favorable for six membered ring formation in such structures. The fact that the straight line in Figure 5 does not pass through the coordinate origin suggests that a similar process may occur also in the 1,4-structure.

*Interaction with sulfur and vulcanization.*—The interaction of rubber with sulfur is the main reaction in the vulcanization process. The reaction of buta-

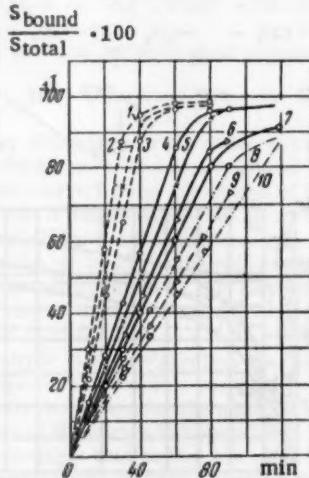


FIG. 6.—Kinetics of sulfur addition to rubbers of 1,4 structure in solution in a nitrogen atmosphere at various temperatures: 1,2,3—155°; 4,5,6,7—142°; 8,9, 10—135°; 1,4,5—SR-6—65%; 2,5—SR-5—60%; 6,9—SR-7—43%; 3,7,10—SR-4—30% of 1,4 structure.

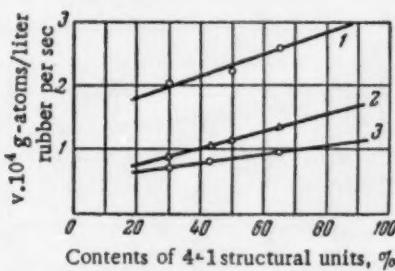


FIG. 7.—Rate of sulfur addition as a function of the rubber structure:  
1—155°; 2—142°; 3—135°

diene polymers with sulfur was studied by heating solutions in toluene in ampoules, with strict exclusion of atmospheric oxygen. The solutions contained about 4 g of rubber per 100 ml of solvent; the sulfur content was 2 g per 100 g of rubber. The accelerator was a condensation product of aniline with acetaldehyde and butyraldehyde (Accelerator A-100), and triethanolamine was used as activator. In the conditions described, addition of sulfur to rubber proceeds at a constant rate for nearly the total duration of the reaction (Figure 6), which may be explained by the large excess of active centers (double bonds and  $\alpha$ -methylene groups) in rubber, in relation to the sulfur, and the narrow variation range of the volume concentration of sulfur in the solution during the entire observation time. As Figure 7 shows, the rate of addition of sulfur to rubber increases linearly with increasing content of the 1,4-structure in the rubber molecules. In the temperature range from 135 to 155° this reaction obeys the Arrhenius equation (Figure 8). The apparent activation energy of the reaction of addition of rubber to sulfur depends on the structure of the polymer, decreasing with increasing content of the 1,4-structure or, which is the same thing, increasing with increasing content of the 1,2-structure (Figure 9). Since this relationship is linear, it is possible by extrapolation to determine the activation energy for a polymer of one particular structure, i.e., to determine the activity of sulfur toward disubstituted double bonds of 1,4-structure and to monosubstituted double bonds of the vinyl side chains of 1,2-structure. Its value in the first case is 14 kcal/mole, and in the second, 19 kcal/mole, and the

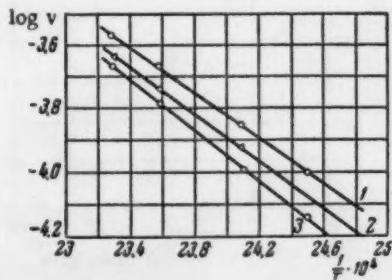


FIG. 8.—Rate of sulfur addition to rubbers of 1,4 structure, as a function of the temperature:  
1) SR-6, 65%; 2) SR-5, 50%; 3) SR-4, 30%.

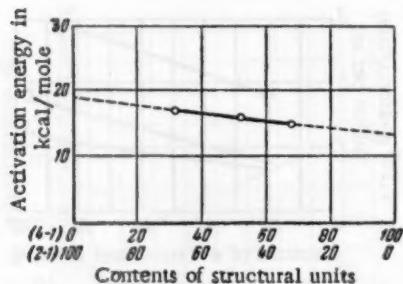


FIG. 9.—Activation energy for the addition of sulfur to rubber as a function of the rubber structure.

difference between these agrees with the corresponding value determined from the kinetics of thermal oxidation of rubbers<sup>7</sup>.

The different chemical reactivities of double bonds of 1,4- and 1,2-structure toward sulfur were established by direct observation of variations of the intensity of the absorption bands in the infrared region of the spectrum during vulcanization. The technique developed for this was reported by Dogadkin and Klausen at the 10th All-Union Conference on Spectroscopy. Rubbers containing 65 and 50% of double bonds of 1,4-structure were studied. The absorption intensity for the 1,4-structure was measured at a frequency of  $965\text{ cm}^{-1}$ , and for the 1,2-structure at  $909\text{ cm}^{-1}$ . The vulcanization was carried out in films applied to rock salt plates, and in solution. In the latter case the spectroscopic determinations were made after evaporation of a sample of the solution placed on a rock salt plate. In the vulcanization experiments in solution, changes of unsaturation were also determined by the reaction with iodine chloride; the results so obtained were in good agreement with the spectroscopic data.

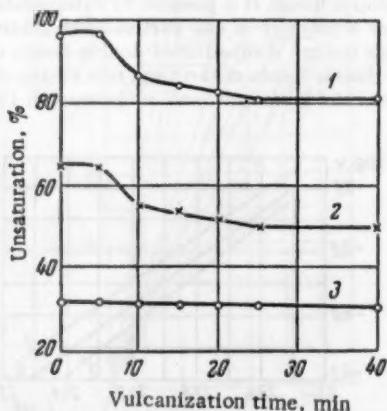


FIG. 10.—Variation of the unsaturation of rubber with 65% of 1,4 structural units during vulcanization in film form in a nitrogen atmosphere at  $142^\circ$ ; 1) total unsaturation; 2) unsaturation of 1,4-structure; 3) unsaturation of 1,2-structure.

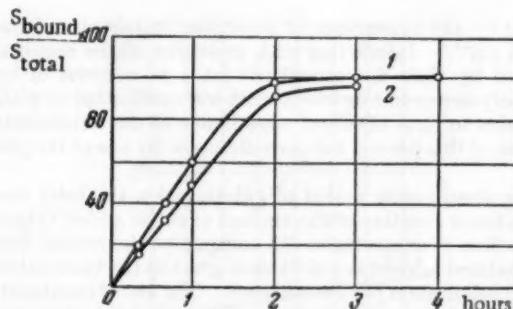


FIG. 11.—Kinetics of sulfur addition to technical rubbers of different structure of the same degree of alkalinity in vulcanization without accelerators in a press at 142°; 1) SR-6, 65% of 1,4-structure; 2) SR-4, 30% of 1,4-structure.

As Figure 10 shows, the double bonds of the 1,4-structure disappear as the result of vulcanization at about 15 times the rate for the double bonds of the vinyl side chains of 1,2-structure. It must be pointed out, however, that this evaluation does not agree with the evaluation based on kinetic data which takes into account the activation energies determined above for the addition of sulfur to 1,4- and 1,2-structures.

If the vulcanization is carried out under technical conditions in a press, the difference between the rates of sulfur addition to rubbers of different structure tends to disappear (Figure 11). The probable explanation for this is the sharp increase of the volume concentration of double bonds, and the consequent increase of the absolute reaction rate, under these conditions in comparison with vulcanization in solution.

It is also significant that, according to spectroscopic data, there is no decrease in the double bond content at the start of vulcanization (horizontal regions in Curves 1 and 2, Figure 10). This means that reactions involving  $\alpha$ -methylene groups of the 1,4-structure predominate at this stage of vulcanization. The reactions involving the  $\alpha$ -methylene groups have different mechanisms. Direct interaction with sulfur leads to formation of thiol groups and displacement of the double bonds into a new position, indicated in the case of

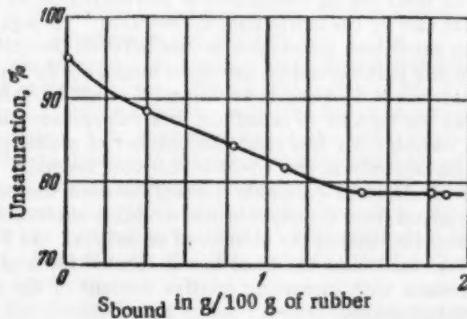


FIG. 12.—Variation of the total unsaturation of SR-5 rubber with addition of sulfur during vulcanization in solution, in a nitrogen atmosphere at 142°.

natural rubber by the appearance of absorption bands at a characteristic frequency of  $965 \text{ cm}^{-1}$ .<sup>8</sup> Interaction with molecules of the accelerator (or with radicals formed by their decomposition) leads to removal of hydrogen and formation of polymeric radicals which react with each other or with the molecular rubber chains to form chemical cross bonds of the vulcanization network. The mechanism of this process has been discussed by one of the present authors elsewhere<sup>9</sup>.

During the steady state period of vulcanization the total decrease of unsaturation is a linear function of the amount of sulfur added (Figure 12). It is found that the loss of unsaturation (in contrast to the results described in the literature for natural rubber) is 4–6 times as great as the value calculated for the addition of one sulfur atom per double bond. The loss of unsaturation increases with vulcanization temperature between 135 and 155°. This increase in the loss of double bonds above the value calculated from maximum substitution with sulfur can be attributed either to polymerization processes involving joining of the molecular chains at the double bonds, or thermal formation of intramolecular rings. The latter hypothesis is refuted by the fact that unsaturation is not changed as the result of prolonged heating (for 12 hours) of rubber and

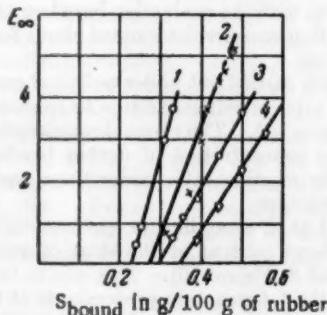


FIG. 13.—Equilibrium modulus as a function of the amount of bound sulfur for rubbers with different contents of 1,4-structural units: 1) SR-6, 65%; 2) SR-5, 50%; 3) SR-7, 43%; 4) SR-4, 30% of 1,4-structure.

its solutions in an inert gas at vulcanization temperatures, as shown both by spectroscopic data and by the iodine chloride reaction. As regards the hypothesis that in these conditions interaction occurs between the sulfur, accelerator, and rubber, inducing polymerization processes analogous to those which occur in the reaction between rubber and benzothiazolyl disulfide<sup>9</sup>, this does not agree with the fact that the number of crosslinks in a vulcanize (determined from the modulus) is considerably less than the number of atoms of bound sulfur. Further experimental study of this effect is therefore needed.

The number of chemical crosslinks formed between the molecular rubber chains was determined from the equilibrium modulus of elasticity  $E$  which, as is known, is a linear function of the number of crosslinks. As Figure 13 shows, the number of intermolecular chemical bonds formed for a given amount of added sulfur increases with increasing relative content of the 1,4-structure in the molecular rubber chains.

The degree of crosslinking  $\Delta E/\Delta S$  is a linear function of the number of double bonds of 1,4-structure (Figure 14). The straight line representing this

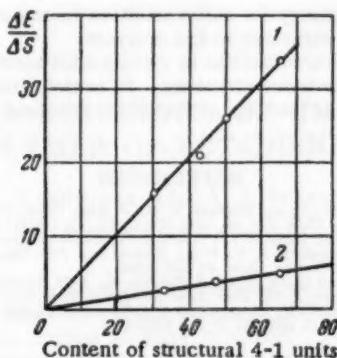


FIG. 14.—Effect of rubber structure on degree of crosslinking; 1) mixture with thiuram;  
2) mixture with mercaptobenzothiazole and sulfur.

relationship passes through the coordinate origin. This shows that, under certain conditions which are determined by an average molecular weight of the rubber at which  $E$  reaches its final value during the first instants of vulcanization, the formation of sulfur bonds in the spatial vulcanization network occurs only in the regions of the chains with 1,4-structure. Since the formation of chemical crosslinks is the main factor in the vulcanization process, this conclusion is of considerable technical significance.

#### SUMMARY

1. Differences between the chemical reactivities of 1,4- and 1,2-structures of butadiene are found in the reactions with perbenzoic acid, iodine chloride, and sulfur.
2. The interaction of perbenzoic acid with solutions of butadiene polymers is represented by kinetic curves with an initial region of a high rate, mainly corresponding to the reaction of the double bonds of 1,4-structure, and a final linear region of a low rate, characterizing the reaction of the double bonds in the vinyl side chains of 1,2-structure. By extrapolation of the linear region to the ordinate axis it is possible to determine the relative contents of the 1,4- (and hence of the 1,2-) structure in the polymer.
3. The kinetic curves for the interaction of the polymer solutions with iodine chloride are of analogous form. The initial region of the kinetic curve represents addition at the double bonds, while the linear region corresponds to the substitution reaction. By extrapolation of the linear region to the ordinate axis it is possible to determine the actual double bond content of the polymer.
4. The kinetic curves for iodine liberation are also of similar form; here the linear region corresponds to the substitution reaction, and the initial region corresponds to the cyclization reaction<sup>6</sup>. The amount of iodine liberated in this reaction is a linear function of the content of the 1,2-structure in the polymer.
5. Mainly the double bonds of the 1,4-structure react when sulfur interacts with the polymer solutions. The total rate of sulfur addition is a linear function of the content of the 1,4-structure.

6. The activation energy for sulfur addition increases with increasing relative content of the 1,2-structure in the polymer.

7. Formation of sulfur crosslinks in vulcanizates occurs mainly as the result of reactions in the 1,4 polymer structure. In consequence, the degree of cross-linking  $\Delta E/\Delta S$  is a linear function of the relative content of 1,4-structure in the polymer.

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# THE CHEMICAL STRUCTURE OF THE "POPCORN" POLYMER OF BUTADIENE \*

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Many investigators have observed that butadiene and its homologs are transformed during storage into white, friable polymers, insoluble in common organic solvents and possessing limited swelling capacity<sup>1</sup>. Formation of a friable butadiene polymer is observed in the large-scale production of butadiene and butadiene-styrene synthetic rubbers<sup>2</sup>.

Our objective in the present work was the study of the structure of this polymer of butadiene in order to elucidate the factors responsible for the lack of rubberlike properties. Friable butadiene polymer was prepared by keeping butadiene in sealed ampoules in a nitrogen atmosphere at 15–20°. These polymerization conditions result in formation of butadiene dimer and two high-molecular polymers of which one is rubbery and soluble in chloroform, benzene and other solvents, while the other is friable, insoluble in organic solvents, and constitutes the main mass (85–90%) of product; we shall call the friable polymer the spongy butadiene polymer in the present paper. Among the products of ozonolysis of the spongy butadiene polymer were found: succinaldehyde, formic acid and formaldehyde; in the form of methyl esters were detected: succinic acid, butane-1,2,4-tricarboxylic acid, and hexane-1,x,y,6-tetracarboxylic acid. Succinic acid and succinaldehyde are formed on ozonolysis from those portions of the macromolecule of spongy butadiene polymer in which the butadiene molecules are linked in the -1,4-1,4- position<sup>3</sup>. Formaldehyde, formic acid and butane-1,2,4-tricarboxylic acid are formed from -1,4-1,2-1,4- portions. The isomeric hexane-1,x,y,6-tetracarboxylic acids, also formic acid and formaldehyde, are formed from -1,4-1,2-1,2-1,4- fragments<sup>3</sup>. The products of ozonolysis of spongy butadiene polymer are set forth in Table I.

In the study of the products of ozonolysis of spongy butadiene polymer, 83.5% of the structure of the carbon skeleton was established: 56.0% of the butadiene molecules are linked in the -1,4-1,4-position; 21.4% are made up of -1,4-1,2-1,4- chains, and 6.1% of -1,4-(1.2)-1,4- portions. 22.8% of chains with external double bonds were found in spongy butadiene polymer. This polymer has the same structure as the rubbery butadiene polymers. The physical properties of the spongy polymer may be governed by the conditions of its formation. A necessary condition for the formation of spongy polymer must be considered to be<sup>4</sup> the presence in the monomer of an insoluble nucleus formed from the polymer or previously introduced into it. (Breitenbach is of the opinion that long, entangled thread-like macromolecules with a gel-like structure are formed in the first stage of development of spongy polymer.) A large number of groups ( $\alpha$ -methylene groups) linked to the nucleus and capable of initiating the growth of chains and participating to a small extent in chain

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TABLE I

Products of ozonolysis	Weight, g <sup>b</sup>	Percentage of carbon skeleton of polymer	Proportion of butadiene units <sup>a</sup>	
			1.4	1.2
Succinic acid	42.50	43.4	43.4	—
Succinaldehyde	1.90	2.1	2.1	—
Dimethyl succinate	13.66	10.5	10.5	—
Trimethyl butane-1,2,4-tricarboxy- late	22.16	21.4	10.7	10.70
Tetramethyl ester of hexane-1,x,y- 6-tetracarboxylic acid	8.66	6.1	2.0	4.06
Total	91.58	83.5	68.7	14.76

<sup>a</sup> The  $\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$  unit is designated 1,4; the  $\text{---CH}_2-\underset{\text{CH}=\text{CH}_2}{\text{CH}}-\text{CH}=\text{CH}_2-$  is 1,2.

<sup>b</sup> Calculated on 50 g of ozonized polymer.

breaking must also be present. Owing to the presence in the active nucleus of a large number of radicals, many macromolecules linked with one another by an insoluble nucleus can grow from a small nucleus.

The insolubility of the spongy polymer may be explained by the insolubility of the nucleus; its friability may be accounted for by the conditions of growth of the nucleus. The latter first swells, then cracks and, finally, breaks up into thin granules. The size reduction of the growing spongy polymer is the result of the growth taking place throughout the whole mass of the nucleus<sup>5</sup>.

The relative content of chains with internal and external double bonds is determined in the soluble butadiene polymer, isolated from the butadiene autopolymer in very small quantity (4.0 g), by oxidation with benzoyl hydroperoxide.

#### EXPERIMENTAL

Butadiene autopolymer is prepared by slow polymerization of butadiene in sealed ampoules in a nitrogen atmosphere in the light at 15–20°. It is a white, friable mass, readily oxidizing in the air; all work with it was therefore performed in a nitrogen atmosphere. From 60 g autopolymer, 5.9 g (9.8%) butadiene dimer was distilled off at 15–20 mm and 40°. B.p. 65–66° at 100 mm,  $d_4^{20}$  0.8312,  $n_D^{20}$  1.4650,  $MR_D$  35.90; Calc. 36.03. Found %: C 98.53; H 11.1.  $C_6H_{12}$ . Calculated %: C 88.89; H 11.11. Found for ethenyl-1-cyclohexene-3;  $d_4^{20}$  0.8320<sup>6</sup>.

Chloroform extraction of the butadiene autopolymer, after separation of the butadiene dimer, gave 4 g (6.4%) of rubbery polymer; the remaining autopolymer (to be designated the spongy polymer) is a white, friable substance, substantially insoluble in common organic solvents and only swelling in them to a slight extent. Found %: C 84.53, 84.70; H 10.74, 10.98. ( $C_4H_6)_x$ . Calculated %: C 88.89; H 11.11.

Ozonization of the spongy polymer of butadiene was effected at –30° with oxygen containing 5–6% ozone in an apparatus ensuring constant concentration of ozone<sup>7</sup>. Only 37% of the polymer was ozonized when the polymer was in the form of a suspension in chloroform. Ozonization in chloroform gives an insoluble ozonide which remains on the surface of the polymer and hinders its further ozonization. This ozonide resinifies to a considerable extent when heated with water. Ozonization goes to completion if the spongy polymer is ozonized in suspension in ethyl acetate, and a colorless, transparent solution of

ozonide is formed. After distillation of the ethyl acetate, the ozonide remains in the form of a colorless, transparent, very viscous substance. This ozonide is decomposed by water without resinification.

The ozonide, destined for elementary analysis, was purified by dissolving in ethyl acetate and precipitating from the solution with ligroine (this procedure was applied three times). Found %: C 45.89, 45.79; H 6.90, 6.90; O 47.21, 47.31.  $(C_4H_6O_3)_x$  Calculated %: C 47.06; H 5.88; O 47.06.

The deviations of the experimental from the calculated values are within the usual limits of error for ozonides; the ozonide of butadiene spongy polymer may therefore be assigned the formula  $(C_4H_6O_3)_x$ .

Products of ozonolysis were prepared for investigational purposes from 50 g of the spongy polymer (containing 42.4 g carbon) in ethyl acetate at  $-30^\circ$ ; 1.5-2 g polymer was ozonized in each experiment. The ozonides were decomposed by heating with water. The aqueous solutions of the products of decomposition of ozonides from the different experiments were combined and the water was driven off, at first at atmospheric pressure (to  $\frac{1}{2}$  of the original volume) and later at 150-100 mm. The product of decomposition of the ozonide was a crystalline substance permeated with a viscous liquid. The crystals were separated with diethyl ether and recrystallized from hot water; m.p.  $183^\circ$ ;

TABLE II

Fraction	Vapor temp.	Weight, g	Calculated from 50 g of ozonized polymer
1	58-61°	8.2	13.66
2	127-130	1.7	} 22.16
3	130-133	11.6	
4	180-190	5.2	
Residue		1.5	2.66
		—	
		28.2	

the melting point of the mixture of the substance with succinic acid was also  $183^\circ$ . The neutralization equivalent of the crystalline acid was 59.2; its anhydride had m.p.  $120^\circ$ . From the products of ozonolysis was isolated 33.7 g succinic acid, containing 13.7 g carbon. Succinaldehyde was detected by the pyrrole test in the distillate coming over with the water. The amount of succinaldehyde in the distillate was determined from the weight of its phenylhydrazone isolated from the solution. The phenylhydrazone melted at 124-125° (from alcohol). The literature gives m.p.  $125^\circ$ <sup>8</sup> and  $124-125^\circ$ <sup>9</sup> for succinaldehyde phenylhydrazone. The aqueous distillate was found to contain 1.9 g succinaldehyde, equivalent to 1.06 g carbon. 56.1 g viscous products of ozonolysis were collected with a carbon content of 44.9%. The 56.1 g viscous products of ozonolysis contained 25.2 g carbon. Properties of aldehydes and acids were detected; evidently a mixture of aldehydes, aldehydo acids and acids is involved. The mixture was oxidized with acetyl hydroperoxide. The latter was prepared from acetic anhydride and concentrated aqueous hydrogen peroxide in presence of sulfuric acid<sup>10</sup>. 91.6% of the products of ozonolysis (containing 22.6 g carbon) was oxidized. 2.7 g carbon were lost in the oxidation. The yield of acids was 89.4%. The product of oxidation was a white, crystalline mass permeated with a colorless, viscous substance. The mixture was

TABLE III

Fraction	Found				Calculated			
	% C	% H	M	Saponification equivalent	$d_4$	$n_D^{20}$	$M_{RD}$	Formula
1	48.9	6.89	148.5	—	73.1	0.1202	1.4190	$\left\{ \text{C}_4\text{H}_{10}\text{O}_4 \right\}$
2	49.1	6.89	146.2	—	—	—	32.90	$\left\{ \text{C}_4\text{H}_{10}\text{O}_4 \right\}$
2	—	—	208.9	—	—	—	—	—
2	49.77	6.64	204.0	68.1	—	—	—	—
3	50.86	6.64	229.8	76.6	—	—	—	—
3	50.70	6.67	235.8	78.6	1.1811	1.4120	51.96	$\left\{ \text{C}_{10}\text{H}_{16}\text{O}_4 \right\}$
4	52.82	6.31	320.4	80.1	—	—	—	$\left\{ \text{C}_4\text{H}_{10}\text{O}_8 \right\}$
4	52.71	6.51	319.6	79.9	1.2195	1.4643	70.00	52.82

\* Literature data: for  $\text{C}_4\text{H}_{10}\text{O}_4$ ,  $n_D^{20} 1.4192^{\text{a}}$ ;  $d_4^{\text{a}} 1.12077^{\text{a}}$ ; for  $\text{C}_{10}\text{H}_{16}\text{O}_4$ ,  $n_D^{20} 1.4446^{\text{a}}$ ; for  $\text{C}_4\text{H}_{10}\text{O}_8$ ,  $n_D^{20} 1.4643^{\text{a}}$ .

separated with ethyl acetate to give 10.5 g succinic acid which melted at 183° after recrystallization; 37.7 g viscous acids were also collected and converted by the action of an ethereal solution of diazomethane into methyl esters of carboxylic acids. The acid esters were separated from the full methyl esters by washing many times with 5% aqueous sodium bicarbonate solution. The full methyl esters were dried with fused sodium bisulfate, and the ethyl acetate was distilled off. 28.2 g full methyl esters were obtained. 4.2 g acid methyl esters were extracted with diethyl ether from the acidified sodium bicarbonate solution. The mixture of methyl esters was fractionated at 2 mm pressure from a flask with a long column; results of the fractionation are given in Table II.

76.3% of the acids (15.7 g carbon) was esterified to give 28.2 g methyl esters instead of the theoretical amount of 38.1 g, i.e., 73.1%. 4.2 g acid esters was isolated. The losses of esters were 5.7 g. The weight of the esters from the products of decomposition of the ozonide from 50 g spongy butadiene polymer was calculated on the basis of the weight of the methyl esters (Table II).

Results of the investigation of the methyl esters of the carboxylic acids obtained from the product of ozonization of the spongy polymer of butadiene are presented in Table III.

Investigation of the methyl esters of the carboxylic acids showed that the first fraction was dimethyl succinate; the analyses of the second fraction indicate

TABLE IV

Weight of rubber ozonized, g	Solvent for ozonization	Per cent starting carbon in the ozonized rubber	Per cent of $C_6H_6$ units with external double bonds
2.5	Chloroform	87.67	34.68
2.5	Ethyl acetate	87.67	34.36

that it is substantially the trimethyl ester of butane-1,2,4-tricarboxylic acid; it apparently contains a small proportion of the previous fraction; the third fraction is the trimethyl ester of butane-1,2,4-tricarboxylic acid; the fourth fraction corresponds to the tetramethyl ester of hexane-1,x,y,6-tetracarboxylic acid.

The ozonized polymer contained 42.4 g carbon. The isolated succinic acid, succinaldehyde, formic acid and formaldehyde represented 19.5 g of the carbon of the polymer. The isolated and characterized methyl esters of carboxylic acids contained 15.7 g carbon. In all, 35.2 g (83%) of the carbon of the polymer was accounted for. The loss of carbon was 7.2 g; of this, 2.7 g was lost during oxidation of the product of ozonolysis with acetyl hydroperoxide; the remaining 4.5 g was in the uninvestigated acid methyl esters and in the residue after fractionation of the full methyl esters of the carboxylic acids.

*Determination of chains with external double bonds in butadiene spongy polymer.*—The method consists in quantitative determination of the formic acid and formaldehyde in the products of ozonolysis of the polymer<sup>13</sup>. This is usually carried out in chloroform. Since the spongy polymer does not undergo ozonization in chloroform, the reaction was carried out in ethyl acetate, the latter solvent, however, is less stable to ozone. In the first place, therefore, comparative determinations were made of formic acid and formaldehyde in the products of decomposition of the ozonide of butadiene rubber after ozonization

in chloroform and in ethyl acetate. On the basis of these data the percentage of chains with external double bonds was calculated. Results are set forth in Table IV and show that reliable results are also obtained with ethyl acetate as the solvent during ozonization.

For the purpose of determination of the chains with external double bonds, 2.3 g spongy polymer was ozonized in ethyl acetate. Formic acid and formaldehyde were determined in the aqueous solution of the products of decomposition of the ozonide, and the percentage of chains with external double bonds was calculated (22.8%).

*Determination of the unsaturation of the chloroform-soluble butadiene polymer isolated from butadiene autopolymer.*—The method described by A. A. Vasilyev<sup>14</sup> was used, based on the reaction of rubber with iodine bromide. Results are presented in Table V.

*Determination of the internal double bonds in the chloroform-soluble butadiene polymer.*—The method of Prilezhaev<sup>15</sup> was applied. This is based on the different velocities of oxidation by benzoyl hydroperoxide of olefinic bonds with different degrees of substitution.

Butadiene rubbers contain  $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$  units (internal double bonds) and  $-\text{CH}_2-\text{CH}(\text{CH}=\text{CH}_2)-$  units (external double bonds). The double bond in the chain containing an internal double bond is oxidized

TABLE V

Polymer, g	Iodine number found without allowance for substitution	Degree of unsaturation of the polymer without allowing for substitution (%)	Iodine number found with allowance for substitution	Unsaturation of the polymer with allowance for substitution (%)
0.0964	435.8	92.7	407.0	86.6
0.0954	435.1	92.7	413.0	86.8

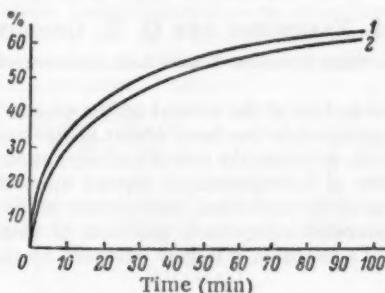
more rapidly than that in the chain with an external double bond. The percentage of internal double bonds is determined from the kinetic curve of oxidation of the rubber with benzoyl hydroperoxide<sup>16</sup>.

Oxidation of the polymer with benzoyl hydroperoxide was carried out in a thermostat at 20°. To 50 ml 0.2 N solution of polymer in chloroform was added 50 ml 0.2 N solution of benzoyl hydroperoxide in chloroform. At definite time intervals 5 ml samples were withdrawn for determination by the iodometric method of the amount of benzoyl hydroperoxide reacted. Parallel samples were taken (5 ml each) from a solution containing only benzoyl hydroperoxide in order to determine the amount of hydroperoxide decomposed. For the purpose of calculation of the percentage of chains with internal double bonds in the polymer in question, oxidation was effected with benzoyl hydroperoxide of butadiene dimer containing double bonds of the same type as those in butadiene polymers. The butadiene dimer was oxidized under the same conditions and with identical ratios of concentrations of the solutions of dimer and hydroperoxide and at the same temperature as in the oxidation of the dissolved butadiene polymer. The curves of rate of oxidation of butadiene dimer and of soluble polymer are plotted in the diagram in which the abscissas represent the times in minutes and the ordinates the per cent of reacted substance. From the curve we find the time in the course of which 50% of the butadiene dimer was oxidized (i.e., the double bond in the ring), and we assume that the

internal double bonds of the butadiene polymer also reacted in the same time. It follows from the diagram that the chloroform-soluble polymer separated from the autopolymer contains 53.5% of chains with internal double bonds and 33.3% of chains with external double bonds.

### SUMMARY

1. The chemical structure of spongy butadiene polymer, obtained at 15–20° was examined by the ozonolysis method.



Curves for rate of oxidation of soluble butadiene polymer (1) and of butadiene dimer (2) by benzoyl hydroperoxide.

2. The per cent of chains with external double bonds in the spongy polymer was found to be 22.8%.

3. The spongy polymer of butadiene is composed, like the rubbery polymers, of chains with external and internal double bonds.

4. It was established that parts of the molecule of spongy polymer have the same structure as the rubbery butadiene polymers: -1,4-1,4-; -1,4-1,2-1,4-; -1,4-1,2-1,2-1,4-.

5. A chloroform-soluble rubberlike polymer was separated from the butadiene autopolymer. The degree of unsaturation of the chloroform-soluble polymer was determined (86.7%), also the relative content of internal and external double bonds.

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## HYDROGENATION OF BUTADIENE RUBBER SOLUTIONS. II. INFLUENCE OF THE SOLVENT WITH PALLADIUM-ON- CALCIUM CARBONATE CATALYST \*

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An influence of the nature of the solvent on the process of catalytic hydrogenation of organic compounds has been observed by many investigators<sup>1-4</sup>. During hydrogenation in solution, the rate of hydrogenation and the percentage transformation (degree of hydrogenation) depend upon the relative adsorbability by the catalyst of the individual components of the system undergoing hydrogenation (unsaturated compound, products of catalytic reaction and solvent); the extent of adsorption is largely governed by the solvent.

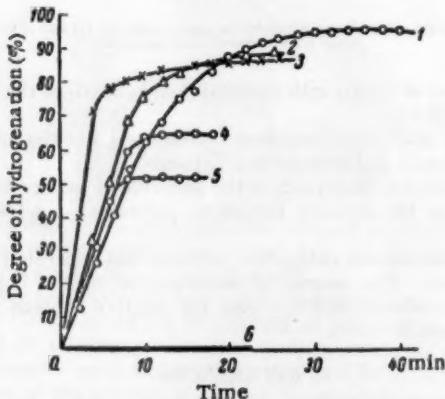


FIG. 1.—Influence of solvent on the degree of hydrogenation of allyl alcohol over palladium-on-calcium carbonate (catalyst 0.2 g., solvent 15 ml.). 1) ethyl ether; 2) heptane; 3) ethyl alcohol; 4) 2,2-dimethyl-dioxane-1,5; 5) isoamyl alcohol; 6) benzene.

With the objective of establishing the influence of the solvent on the rate and extent of hydrogenation of an unsaturated compound in presence of palladium-on-calcium carbonate catalyst, we carried out the hydrogenation of allyl alcohol with this catalyst in various solvents. Results are plotted in the diagram.

Figure 1 indicates that the solvent exerts a marked influence not only on the rate of hydrogenation of allyl alcohol over palladium-on-calcium carbonate catalyst (the slope of the initial portion of the curve), but also on the degree of

\* Translated from the *Zhurnal Obrabotki Khimii*, Vol. 26, pages 1626-1628 (1956).

hydrogenation. Thus, for example, in ethyl alcohol and heptane (Curves 2 and 3) in presence of 0.2 g of the catalyst, allyl alcohol is hydrogenated to the extent of approximately 87 per cent, in isoamyl alcohol (Curve 5) to the extent of 52 per cent, in 2,2-dimethyldioxane-1,5 (Curve 4) to the extent of 65 per cent, in diethyl ether (Curve 1) to the extent of 95 per cent. Allyl alcohol does not undergo hydrogenation in benzene (Curve 6).

In the S. V. Lebedev Laboratory at the Leningrad State University it was established that increase of polarity of the solvent (addition of ethyl alcohol to pentane in the system being hydrogenated) leads to a rise in the degree of hydrogenation of diallyl over palladium-on-calcium carbonate from 84 to 100 per cent. It may be expected that by a suitable selection of catalyst and solvent the process of hydrogenation of rubber might be realized with greater facility and with a smaller consumption of catalyst<sup>5</sup>.

On the basis of the foregoing considerations, it was resolved to investigate the process of hydrogenation of rubber in a solvent whose chemical character differed from heptane. The solvent chosen was 2,2-dimethyldioxane-1,5 (DMD). For removal of peroxy compounds, DMD was kept for 24 hours in presence of hydroquinone and distilled in presence of hydroquinone in a nitrogen atmosphere; it then had b.p. 133–134° and  $n_D^{20}$  1.4230.

TABLE I  
PROPERTIES OF HYDROGENATED BUTADIENE RUBBER OBTAINED WITH  
PALLADIUM-ON-CALCIUM CARBONATE CATALYST IN  
2,2-DIMETHYLDIOXANE-1,5

Specimen	Per cent hydrogen added	Hydrogenated rubber	Unsaturation, %	Per cent internal double bonds	$n_D$	Relative viscosity (0.08% benzene solution)	Vitrification temperature
—	0	—	86.2	38.0	1.5120	1.310	-60.0°
1	56.4	From solution	—	36.5	1.5065	1.315	—
2	22.9 {	From solution	84.4	37.0	1.5120	1.313	—
3	81.3	From catalyst	8.0	9.5	1.4820	1.154	—
4	50 {	From catalyst	7.6	—	1.4824	1.185	-71.7
		From solution	84.1	—	1.5118	1.320	—
		From catalyst	2.7	—	1.4802	1.148	—

Hydrogenated butadiene rubber was insoluble in DMD; during hydrogenation in presence of palladium-on-calcium carbonate, the hydrogenated product therefore remained on the surface of the solvent. A 30-fold amount of catalyst was needed to hydrogenate the whole of the initial rubber in DMD. Part of the original rubber remained in solution when insufficient catalyst was used; this could be judged by data for determination of the degree of unsaturation, the content of internal double bonds, the refractive index and the relative viscosity of the benzene solution of the rubber recovered from solution.

In order to evaluate the selectivity of the hydrogenation of the double bonds of the rubber in DMD, the rubber was hydrogenated to the extent of 50 per cent. Results showed, however, that although an adequate amount of catalyst was used, not all the rubber was 50 per cent hydrogenated. Rubber washed out from the catalyst with benzene had 8 per cent unsaturation; rubber isolated from solution had 84.4 per cent unsaturation.

Results obtained with DMD are presented in the Table I.

In the case of hydrogenated butadiene rubber obtained with palladium-on-calcium carbonate catalyst in DMD (washed out of the catalyst with benzene)

the same relation between degree of hydrogenation and properties is observed as that established for hydrogenated rubber obtained in heptane with the same catalyst: fall in relative viscosity of benzene solutions, fall in refractive index and lowering of the temperature of vitrification of the rubber with increasing degree of hydrogenation. The absence of outer double bonds in hydrogenated rubber with 8 per cent unsaturation (judging by data for the internal double bonds) indicates that the outer double bonds are hydrogenated more rapidly than the internal bonds.

It is noteworthy that in the case of hydrogenated rubber with 8 per cent unsaturation, obtained in DMD, the percentage of residual internal double bonds is about the same as the unsaturation and amounts to 9.5 per cent, whereas in the case of hydronrubber obtained in heptane and with a percentage unsaturation<sup>5</sup> of 11.6 per cent the percentage of residual internal double bonds is 5.5 per cent. The difference in selectivity of the hydrogenation of double bonds in rubber which was detected during hydrogenation in heptane and DMD is evidently due to the heterogeneity of the hydronrubbers examined. It is very probable that the product of hydrogenation of rubber (a high-molecular weight, unsaturated hydrocarbon comprising a mixture of polymer homologs) is not, strictly speaking, homogeneous, and that the degree of unsaturation of its individual molecules may vary. The main mass of hydrogenated rubber may contain molecules of different degrees of hydrogenation and even, in some cases, molecules of unchanged rubber. In this respect the product of partial hydrogenation of rubber is an even more complex mixture of molecules of different sizes and different compositions from the original rubber.

During the hydrogenation of rubber in heptane, the hydronrubber formed at the surface of the catalyst mainly goes into the solution, as can be inferred from the degree of unsaturation found for the hydrogenated rubber and from the amount of hydrogen taken up by the rubber. In DMD, the hydrogenated rubber remains on the catalyst. Consequently, in specimens of partially hydrogenated rubber obtained in heptane, we have a mixture of hydrogenated and nonhydrogenated molecules of rubber; in specimens obtained in DMD, we have only hydrogenated molecules, since the nonhydrogenated rubber remained in solution. For this reason we obtained slightly differing results in the study of the selectivity of hydrogenation of the double bonds in heptane and in DMD.

#### SUMMARY

Experiments with allyl alcohol demonstrated the influence of the nature of the solvent on the speed and degree of hydrogenation of an unsaturated organic compound on palladium-on-calcium carbonate catalyst.

Butadiene rubber was hydrogenated on palladium-on-calcium carbonate in 2,2-dimethyldioxane-1,5 (DMD), and specimens of hydronrubber insoluble in that solvent were obtained.

The same relation between degree of hydrogenation and properties was found for hydronrubber obtained with palladium-on-calcium carbonate catalyst in 2,2-dimethyldioxane-1,5 as had been established for hydronrubber obtained in heptane with the same catalyst: fall in relative viscosity of benzene solutions, lowering of refractive index, and fall in the temperature of vitrification of the rubber with increasing degree of hydrogenation.

The selectivity of hydrogenation of the outer double bonds of butadiene rubber when hydrogenated in 2,2-dimethyldioxane is more clearly manifested than in the case of hydrogenation in heptane.

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## TWO STAGES IN THE PROCESS OF NETWORK FORMATION IN POLYMERS\*

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The crosslinking (structurization) of linear and slightly branched polymers forms the basis of a number of technological processes, of which the most important are: vulcanization of rubber, tanning of collagen and gelatin, and hardening of thermosetting resins. These structurization processes, in contrast to aging processes, can be regulated and they play an important part in the manufacture of materials with certain required network structure and properties. The structurization processes which occur in aging develop spontaneously and in most cases have an adverse effect by changing the desired structure and degrading the properties of the materials.

It has been shown that the process of spatial network formation occurs in two stages. The two-stage nature of the process was observed in the first two

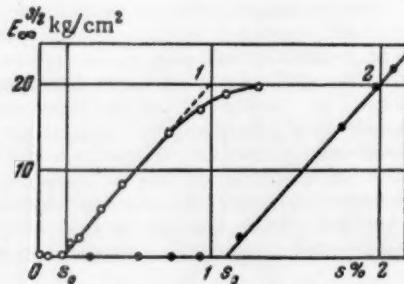


FIG. 1.—Relationship between the equilibrium modulus and the amount of bound sulfur (in weight percentages on the vulcanizate): 1) NR (natural rubber); 2) SKS-30A.

investigations<sup>1,2</sup>. In the third<sup>3</sup>, the importance of the initial molecular weight of the polymer was established. It was shown that the start of network formation corresponds to a certain quite definite amount of bound sulfur, which depends on the molecular weight of the polymer. The first general views on the two-stage nature of the process were probably put forward by Flory<sup>4</sup>.

The general mechanism of spatial network formation in the structurization of linear polymers, for the case of rubber vulcanization, is discussed below. The chemical aspects of polymer network formation are discussed in a recent review<sup>5</sup>.

The two-stage nature of the network formation process is seen in Figure 1, which shows, as an illustration, the variation of the equilibrium modulus (to the

\* Reprinted from *Colloid Journal (USSR)* 19, 267-272 (1957); translated by Consultants Bureau, Inc. from *Kolloidnyi Zhurnal*, Vol. 19, 261-267 (1957).

power 3/2) with the amount of sulfur bound during vulcanization of an unfilled natural rubber composition (NR), of molecular weight 150,000, modulus at 20°, from N. M. Novikova's data, and a synthetic SKS-30A rubber fraction of molecular weight 140,000, modulus at 70°, from the data of F. A. Galil-Ogly. The choice of the equilibrium modulus to characterize the spatial network<sup>6,7</sup> is explained by the fact that the equilibrium modulus  $E_\infty^1$  bears a definite relationship to the number of chains in the network,  $N$ , per unit volume. In Figure 1, values of  $E_\infty^1$ , which, according to Bartenev<sup>6</sup>, are proportional to  $N$ , are taken along the ordinate axis. If the amount of bound sulfur is proportional to the number of crosslinks, then the relationship between  $E_\infty^1$  and the amount of bound sulfur must be linear; this is found to be so for all fractions of SKS-30A at the second stage of crosslinking<sup>8</sup>. Natural rubber shows a deviation from linearity at the end of the second stage; this is explained by superposition of thermo-oxidative degradation processes on vulcanization.

At the first stage a single spatial network is not yet formed, as the equilibrium modulus is zero. At the first stage the material is in a plastic, and at the second, in an elastic state. At the first structurization stage the molecular chains are not yet joined in a single spatial network, but individual molecules are crosslinked into larger formations. Only after these molecular aggregates have reached a definite size does the subsequent crosslinking lead to the formation of a continuous spatial network.

Let us consider the crosslinking of a linear polymer with initial molecular weight  $M_0$ , assuming that the crosslinks have a statistically uniform distribution throughout the volume. Let  $M$  be the molecular weight of a chain in the network (segment of a linear molecule between two crosslinks). Corresponding to these are  $N_0$  and  $N$ , the numbers of original molecules and network chains per unit volume;  $n$  is the total number of crosslinks per unit volume of the polymer;  $\nu$  is the number of effective crosslinks per unit volume.

At the first stage of structurization the crosslinks join individual linear molecules, which results in an increase of the average molecular weight of the polymer. As has been reported<sup>1,4,8</sup>, network formation begins not at once, but after all (or nearly all) the molecules of the original material have been joined by crosslinks. At this stage long branched chains are formed, much larger than the original linear molecules. Thus, crosslinking of individual molecules leads to formation of long branched chains, the molecular weight  $M$  of which increases to values greatly exceeding  $M_0$ .

The material remains plastic until enough crosslinks have been formed to join the original molecules into a spatial network. We shall term this number of crosslinks per unit volume the "critical" number, and shall denote it by  $n_k = \beta N_0$ , where  $\beta$  is a coefficient which depends on the molecular weight distribution, and the degree of coiling and intertwining of the molecules in the original material (the meaning of the coefficient  $\beta$  is discussed below).

It is evident that when  $n < n_k$ ,  $\nu = 0$ ; when  $n \geq n_k$ ,  $\nu = n - n_k$ .

The number of chains  $N$  determines the equilibrium properties and is included in the formulas of the molecular theory of network polymers. Since each new crosslink forms two new chains,  $N = 2\nu$ , and therefore when  $n > n_k$

$$N = 2(n - n_k) = 2(n - \beta N_0) \quad (1)$$

and when  $n < n_k$ ,  $N = 0$ .

The Flory formula<sup>4,8</sup> derived (for  $\beta = 1$ ) with network defects (terminal chains) taken into account

$$N = \frac{\rho_0 N_A}{M} \left( 1 - \frac{2M}{M_0} \right)$$

is not suitable for the whole  $n \geq n_k$  range of network formation. The formula is approximately correct when  $M \ll M_0$ , that is, for dense networks and high original molecular weights. In practice these conditions are probably satisfied for network polymers with molecular weight  $M_0 > 10^5$  and equilibrium modulus  $E_\infty$  greater than  $10 \text{ kg/cm}^2$ .

The general formula, valid over the entire  $n \geq n_k$  range has the following form

$$N = 2n \left/ \left( 1 + \frac{2\beta\rho M}{\rho_0 M_0} \right) \right.$$

where  $\rho$  is the density for the active part of the rubber;  $\rho_0$  is the density for the

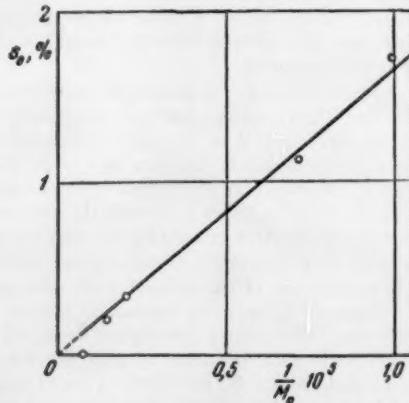


FIG. 2.—Relationship between the "critical" amount of sulfur added during vulcanization, and the reciprocal molecular weight of the original polymer (from data in <sup>5</sup>).

whole rubber, including the regions of the molecules which did not enter the network. Calculation of  $\rho$  is the main difficulty in the use of this formula.

To illustrate the application of these relationships, let us consider the vulcanization of butadiene-styrene SKS-30A and natural (NR) rubber. Let  $j$  be the number of sulfur atoms per crosslink both between different molecules and between parts of the same molecule. The total and "critical" numbers of crosslinks are expressed in terms of the amount of bound sulfur by the following formulas:

$$n = \frac{\rho N_A}{\mu j} \frac{s}{100}; \quad n_k = \frac{\rho N_A}{\mu j} \frac{s_0}{100} \quad (2)$$

where  $\mu = 32.1$  is the atomic weight of sulfur;  $s$  and  $s_0$  are the total and "critical" amounts of bound sulfur in percentages by weight (on the vulcanizate).

For the "critical" amount of bound sulfur we have the formula

$$s_0 = \beta j \mu \cdot 100 \frac{1}{M_0} \quad (3)$$

which is in good agreement with the data<sup>3</sup> given in Figure 2.

The value of  $s_0$  is determined from the intercept cut off (Figure 1). For NR,  $s_0$  is 0.15% at  $M_0 = 150,000$ , which gives  $\beta j = 7$ . For SKS-30A the value, found from the straight line in Figure 2, is  $\beta j = 50$ .

It is not possible to determine the number of sulfur atoms in the crosslink,  $j$ , by the intercept method, as the coefficient  $\beta$  is not known. It is possible to find  $j$  from the slope of the straight line in the coordinates of Figure 1.

From Equations (1) and (2) it follows that

$$N = \frac{2\rho N_A}{\mu j} \frac{\Delta s}{100} \quad (4)$$

where  $\Delta s = s - s_0$ .

For further calculations by this formula it is necessary to know the relation-

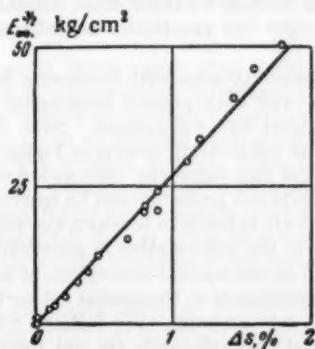


FIG. 3.—Variation of equilibrium modulus with the amount of bound sulfur added in the second stage of vulcanization, for different fractions of SKS-30A rubber with molecular weights from 100,000 to 1,170,000, from F. A. Galil-Ogly's data (equilibrium modulus determined at 70°).

ship between  $N$  and  $E_m$ . For this we use the relationship  $N = CE_m^{\frac{1}{m}}$ , where  $C$  is a constant which depends on the physical properties of the polymer molecules and the temperature.

This constant can be calculated if the length of the chain segment in the Kuhn model is known. According to Vishnitskaya, for NR  $l = 12.0$  Å (according to Kuhn  $l = 13$  Å), and for SKS-30A  $l = 12.6$  Å.

Figure 1 gives data for NR at 20° and for SKS-30A (fraction of molecular weight 140,000) at 70°. For these temperatures, calculation of the constant gives the following values:  $C = 2.29 \cdot 10^{18}$  for NR, and  $C = 1.96 \cdot 10^{18}$  for SKS-30A, if the equilibrium modulus is expressed in kilograms per cm<sup>2</sup>.

Using the numerical values of the quantities in Formula (4) ( $\rho = 0.96$  for NR,  $\rho = 0.94$  for SKS-30A vulcanizates), we find from the slopes of the straight lines in Figure 1 (for NR) and Figure 3 (for SSK-30A) that  $j \approx 7$  for both rubbers.

At first sight, a very simple conclusion suggests itself: each crosslink is formed by the opening of an eight-membered sulfur ring, as in vulcanization without accelerators<sup>9</sup>. However, this cannot be asserted, in view of the possible deviations from the ideal vulcanization process. There are data<sup>9</sup> showing that  $j$  should be smaller in vulcanization with an accelerator. It must be taken into account that part of the added sulfur does not form crosslinks<sup>1</sup>, and this may lead to a decrease of  $j$ . From the experimental results given (Figures 1, 3, 4) it follows that the amount of sulfur which does not form crosslinks is proportional to the total amount of bound sulfur.

Network defects (in contrast to the ideal network formed by crosslinking of a linear polymer of the maximum molecular weight) include closed loops, ends of molecules not included in the network, mechanical entanglement of two chains (according to Flory<sup>4</sup>), crosslinks in close proximity to each other, and branching of the polymer chains. These "defects" can be taken into account only roughly and qualitatively. It has been shown for NR<sup>6</sup> that the ends of the original rubber molecules which do not enter into the network do not influence the equilibrium modulus if the initial molecular weight is high enough (150,000) and the modulus is not too low. It is evident that defects like ends and closed loops depend on the initial molecular weight. It follows from the data in Figure 3 that for SKS-30A rubber these defects are not significant, as the initial molecular weight has practically no influence on the equilibrium modulus.

Crosslinks in close proximity arise with increasing frequency as the spatial network becomes denser and with greater irregularity of distribution of the sulfur molecules throughout the vulcanizate. Such defects should lead to deviations from the linear relationship shown in Figure 3 only with high contents of bound sulfur. For thin networks, such as are represented by the data in Figures 1-3, these defects can probably also be ignored. If ends, loops, and closely situated crosslinks are taken into account, the value of  $j$  should decrease (to only a slight extent for the vulcanizates in question).

Other "defects", such as mechanical entanglement and branching, result in formation of additional crossbonds in the spatial network and therefore  $j$  would increase if they are taken into account. For NR and SKS-30A branching may be neglected. Mechanical entanglements are not fixed crosslinks in the network, as the points of contact continuously change because of thermal motion. These have not been taken into consideration in the deformation theory of network polymers.

The views put forward above provide an explanation for the "critical" molecular weight of rubber, below which the first vulcanization stage is not found<sup>8</sup>. The material before vulcanization usually contains a certain number  $n'$  of crosslinks of various origins. With a high enough molecular weight of the rubber this number may reach the critical value, and the critical molecular weight is therefore  $M'_0 = \beta\rho N_A/n'$ .

The different coefficients for NR and SKS-30A ( $\beta = 1$  and  $\beta = 7$ ) were somewhat unexpected. The probable explanation for the difference lies in the technological preparation of the materials for vulcanization. Fractions of SKS-30A rubber were prepared in the form of films from a solution of the rubber and other ingredients in benzene, while the natural rubber mix was made in the usual way on mill rolls. The same result as for NR ( $\beta = 1$ ) was obtained for SKS-30A and SKS-30 mixes made on mill rolls. This probably indicates that the molecules become globularized in solution<sup>10</sup>, in contrast to mill processing, where

the chain molecules become ruptured and entangled. In this case the molecular weight  $M_0$  refers not to the original rubber but to the material after milling.

In a globular structure a considerable proportion of the crosslinks is used in intramolecular crosslinking, which prolongs the first structurization stage.

In rubber technology attention has been devoted mainly to studies of the vulcanization optimum. The initial stage of vulcanization has been studied only recently. In two investigations<sup>11,12</sup> the conditions and duration of the initial stage of vulcanization were studied both from the technological and the chemical aspects (chemical kinetics of crosslink formation).

The first vulcanization stage determines the correct technological production of molded rubber articles. The flow of the rubber mix and filling of the mold depend on the existence of this stage. The pressure in the vulcanization press and in pressure molding makes for a more rapid filling of the mold. Absence of the first vulcanization stage leads to the undesirable effect known as "scorching". At vulcanization temperatures (130–150°), as has been shown<sup>9,13,14</sup>, irreversible flow occurs in network polymers also, but the rate of plastic deformation at the second vulcanization stage is low and the mold is filled mainly during the first stage of the process.

The duration of the first vulcanization stage  $t = \int_0^* \frac{ds}{W}$  depends on the sul-

fur addition rate  $W = ds/dt$ , critical amount of sulfur  $s_0$ , and therefore on the type of accelerator group, vulcanization temperature, technological preparation, and the molecular weight of the starting material. Absence of the first vulcanization stage is a result of the fact that a critical or larger number of crosslinks is formed in the original material before vulcanization, owing to thermooxidation processes, scorching, and other structurization processes. The existence of a prolonged first vulcanization stage (like its absence) is undesirable, and is caused by a low rate of sulfur addition, low molecular weight, absence of high molecular weight fractions in the rubber, globular structure of the polymer, etc.

Correct technology of vulcanization of rubber mixes in molding presses should correspond to a quite definite optimum duration of the first stage of the process. At present the composition of the technological rubber mixes for the production of molded articles is based on the results of practical experience. Therefore the technological potentialities will be increased by the use of a method whereby the duration of the first stage can be determined.

The duration of the first stage can be determined by measurement of the equilibrium modulus for different times of vulcanization of the mix. The non-equilibrium (technological) modulus is unsuitable for this purpose, as it is not zero for the plastic state. As an illustration, Figure 4 shows the variation of the equilibrium modulus with vulcanization time for an unfilled mixture made on rolls from SKS-30 rubber with 3 parts of sulfur and 1 part of mercaptobenzothiazole by weight, at a vulcanization temperature of 143°.

At the present time the optimum value of the first vulcanization stage is chosen indirectly by plasticity tests on the mixes and by selection of rubbers of suitable molecular weight distribution, by addition of antioxidants, and by suitable selection of vulcanizing systems, mixing conditions, and vulcanization temperature. The simultaneous presence of fractions of low and high molecular weight ensures plasticity of the mixture at the first stage and a high rate of network formation at the second stage.

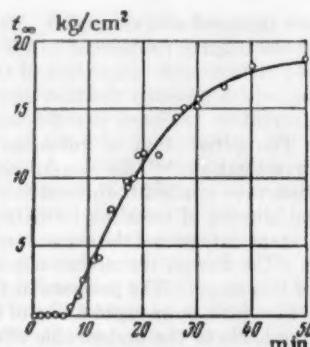


FIG. 4.—Variation of the equilibrium modulus with vulcanization time for unfilled SKS-30 rubber, from published data<sup>2</sup>.

The effectiveness of the proposed method should be verified by further investigations on technical rubbers. Applications of the method to studies of structurization processes in gelatin and resins<sup>15,16</sup> are of undoubtedly interest.

#### SUMMARY

1. The two-stage nature of network formation in polymers is discussed, and a formula is derived connecting the number of chains in the network with the initial molecular weight of the polymer and the number of crosslinks. It is shown that below a certain critical number of crosslinks a network is not formed.

2. The application of the derived relationships in determination of the number of sulfur atoms in the crosslinks, the critical molecular weight, and the degree of globulization of the rubber, has been studied in the case of rubber vulcanization.

3. The first vulcanization stage is shown to be of considerable practical importance, as it determines the correct technological conditions for the vulcanization of rubber in molding presses, multilayer articles, etc. For this reason, determinations of the vulcanization optimum in rubber technology must be augmented by studies of the initial stage of the process. A method for determining the duration of the first stage of vulcanization is described.

#### ACKNOWLEDGMENT

I express my gratitude to B. A. Dogadkin for discussion of the work.

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# MODERN THEORIES OF RUBBER RECLAIMING \*

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## INTRODUCTION

As early as 1858, Hiram L. Hall patented the use of higher temperatures for the purpose of plasticizing vulcanized rubber, and while very substantial improvements in its utilization have been effected, this treatment together with a varying degree of subsequent mechanical working, still serves in most present day reclaiming processes. Fabric removal is normally achieved concurrently with the thermal treatment. Operating conditions are outlined below:—

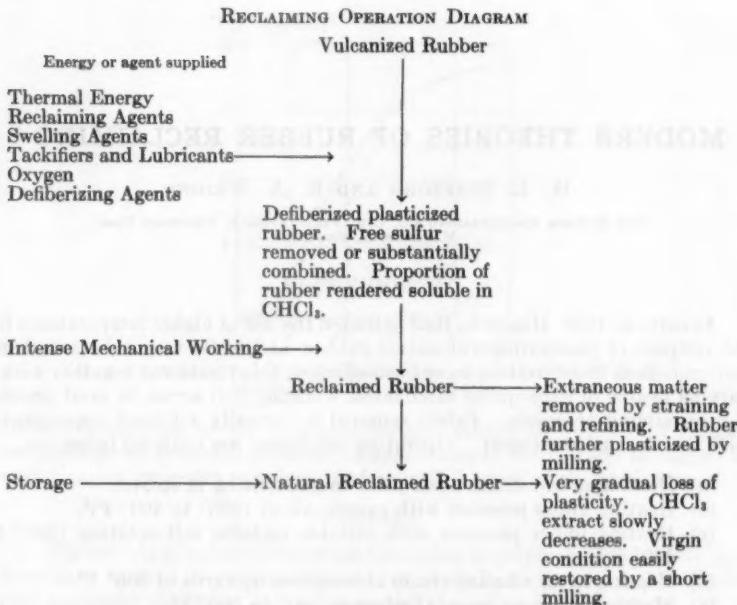
- (a) Heating in hot dilute acids prior to plasticizing in steam<sup>1</sup>.
- (b) Heating under pressure with caustic alkali (360° to 400° F)<sup>2</sup>.
- (c) Heating under pressure with suitable metallic salt solution (360° to 400° F)<sup>3</sup>.
- (d) Heating in an alkaline steam atmosphere upwards of 400° F<sup>4</sup>.
- (e) Mastication in an internal mixer at 400° to 500° F<sup>5</sup>.
- (f) Exposure to acid vapors<sup>6</sup>.
- (g) Biological methods<sup>7</sup>.

The defiberized plasticized waste is converted to finished reclaim by a process of "massing," straining and final passage through tight set refiner rolls. Ignoring modifications and additions made to induce specific characteristics in the ultimate product, thermal plasticization can be regarded as a prerequisite of subsequent milling, etc., and is devised to achieve maximum quality and productivity. While the processes of reclaiming induce profound changes of rubber structure, etc., superficially reclaim can be regarded as being closely related in composition to the vulcanized scrap of origin, but possessing sufficient plasticity to admit of remolding, etc. Since most commercial processes employ the common factor of high temperatures, reclaim hydrocarbon can be regarded as having properties characteristic of its class.

Orthodox reclaiming could be briefly shown by the diagram at top of p. 600.

*Fundamentals of thermal treatment.*—Vulcanization is commonly regarded as involving the crosslinking of primary polymer chains resulting in a network structure and can be envisaged as a polymerization process. The relatively high temperatures commonly used in reclaiming (360° to 400° F) induce far-reaching and complex molecular breakdown, which can be looked upon as essentially one of depolymerization. The degree of breakdown is considerably influenced by such factors as heating media, composition of vulcanizate, temperature, time, etc. The type of polymer is of particular importance, for example, the well-known "marching" modulus of GR-S implies difficulties in thermal depolymerization. The strong surface forces of reinforcing pigments,

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together with any increase in thermal stability necessitate modifications in the treatment afforded. Tire treads are, for example, more difficult to plasticize than red motor tubes. Winkelmann and Stafford<sup>8</sup> were among the first to show that reclaiming caused up to 50 per cent of the rubber hydrocarbon to be rendered chloroform soluble and that the soluble rubber has a lower sulfur content than the insoluble. The extent of chloroform solubility is regarded as a rough index of the degree of "molecular cracking" induced, and this rather viscous fluid no doubt contributes materially to the physical plasticizing of the much tougher insoluble rubber. On the other hand, the ratio of soluble to insoluble is not a reliable means of assessing the "workability" of the ultimate reclaim and this suggests that other chemical and physical changes are important<sup>9</sup>.

*Consideration of reversion as applied to reclaiming.*—There are obvious analogies between reclaiming and reversion. It has been suggested that the reaction responsible for reversion sets in at the start of cure, and that modulus measures the net effect of crosslinking minus reversion<sup>10</sup>. The high temperatures used in reclaiming rapidly cause the residual free sulfur to combine, this being followed by a process similar to reversion. Uma Shankar<sup>11</sup> studied reversion and concluded that breakdown of crosslinkages, including polysulfides, predominates over any simultaneous formation and that exclusion of oxygen will not prevent reversion if the temperature is high enough to supply the necessary energy to break up the crosslinks.

There are grounds for believing that heating above certain temperatures will increase the ratio of cyclic to polysulfide linkages. P. J. Flory, W. Rabjohn and M. C. Schaffer<sup>12</sup> suggest that the decrease in tensile strength accompanying

prolonged cure could not be attributed to a modification of the chain units, but rather to the continued formation of crosslinkages, the occurrence of chain scission or both. On heat aging, the latter becomes excessive. Reversion may be partly attributed to the rupture of previously formed crosslinks.

R. L. Zapp, R. H. Decker, M. S. Dyroff and H. R. Rayner<sup>13</sup> vulcanized butyl rubber with sulfur, etc., at various temperatures between 250° to 400° F. As may have been anticipated, reversion was more pronounced at higher curing temperatures and was accompanied by high zinc sulfide formation, and an increased combined sulfur per crosslink. Investigation has shown that unvulcanized butyl rubber showed no decrease in molecular weight on heating 10 minutes at 400° F, this and other evidence indicating that the increased swelling in solvents observed with the progress of reversion, was the result of the rupture of disulfide crosslinks. F. P. Baldwin, L. B. Turner and R. L. Zapp<sup>14</sup> suggest that hydrogen sulfide is partially responsible for the reversion of butyl vulcanizates.



These very brief references on the subject of reversion suggest that the relatively severe thermal conditions used in reclaiming would induce extensive molecular chain scission, together with profound changes in the combination of sulfur or other crosslinkages which are responsible for conferring the characteristics of vulcanization. Both these changes can be expected to reduce the resistance to deformation and to render the original vulcanized rubber more responsive to the intense milling which follows the thermal treatment.

G. F. Bloomfield<sup>15</sup>, discussing the structure of vulcanized rubber indicates that only those sections of the molecular chains which are confined between the crosslinks can resist deformation. As pointed out, this is an idealistic explanation, but it can readily be seen that if reclaiming induces the breaking of chains between the crosslinks then there will be large increases in the extent of free ends which, of course, cannot resist deformation. This change towards a more plastic condition will be further increased by any rupture of the crosslinks, though it is possible that there may be a recombination of sulfur in an intramolecular form with consequent modification of the structure of the ultimate reclaim. However, assuming that the process of reclaiming is essentially one of depolymerization it is customary to regard reclaim as being made up of fragmentary molecules. At all events, all commercial reclaims have residual elasticity thus indicating that combined thermal and mechanical working have not completely removed the characteristics of vulcanization. The reversion reaction does not appear to be readily completed.

*Influence of conditions of heat application and nature of molecular breakdown.*—According to the necessity or otherwise of destroying fiber, and dependent upon the ultimate type of reclaim required, commercial processing involves the use of various surrounding media, during the thermal treatment, e.g., water, steam, alkali, metallic salt solution, etc., and usually small ratios of oxygen. There is strong evidence that the presence of the latter plays a vital role in the mechanism of the softening process<sup>16</sup>. It is suggested that this proceeds through a process whereby active radicals result from the application of thermal energy, followed by hydroperoxidation of the hydrocarbon chain and subsequent breakdown with consequent depolymerization. D. S. LeBeau<sup>17</sup> using a temperature of 196.6° C and up to 16 hours heating time, found certain specific differences in the physical and chemical changes dependent upon the medium used. As

already indicated, reclaiming conditions result in a proportion of the original vulcanizate becoming highly depolymerized and soluble in chloroform and the extent of this change, with certain reservations, is accepted as a measure of the degree of molecular breakdown. This was found to be greater after treatment with alkali and steam than with water or metallic salt solution. Antioxidants, as may be expected, somewhat decreased the breakdown rate. Losses in unsaturation and increases in acetone extract, while significant in some instances, were generally of a low order. It was concluded that hydroperoxidative breakdown accompanied commercial reclaiming and that any secondary oxidation was only incidental. The influence of oxygen was described as temporary and this received additional support from an investigation based upon infrared spectrography<sup>18</sup>. The hydroperoxidative breakdown in reclaiming may not follow exactly the same course as with unvulcanized rubber. G. F. Bloomfield<sup>19</sup>, in a paper on the oxidative breakdown of rubber, pointed out that whereas with vulcanized types initial oxidative attack probably involves hydroperoxidation, there may well be oxidation of the sulfide linkages.

*Aids to thermal plasticization.*—In the technical operation of reclaiming it is usual to make suitable additions with the object of increasing thermal plasticization and to confer specific properties on the ultimate product. Very broadly these fall into three groups:

- (1) Swelling agents (relatively volatile and not completely retained in the ultimate reclaims).
- (2) Tackifiers and lubricants.
- (3) Reclaiming agents.

*Swelling agents.*—These include terpene hydrocarbons, naphthas, etc., and while they are normally substantially eliminated after the removal of the charge from the autoclave, they do have a profound influence on speeding up and amplifying depolymerization<sup>18</sup>. This is amply proved by the chloroform extracts. It has also been shown that the efficiency of naphthas appeared to be linked with the auto-oxidative susceptibility, certain constituents, e.g., indene, di-cyclopentadiene, etc., being especially effective. There seems to be no doubt that the increased efficiency induced by certain swelling agents results from chemical rather than physical changes.

J. R. Scott<sup>20</sup>, in a study of the swelling of vulcanized rubber by various solvents, identifies "swelling increment" which, it is suggested, results from chemical action involving depolymerization with the aid of oxygen. Turpentine and decalin both show high increments and are good swelling agents. There may be some parallel between reclaiming efficiency and swelling increment, e.g., certain organic bases increase swelling increment and likewise some bases are effective reclaiming aids. Water was found to reduce swelling increments, a finding said to be in accord with the effect of water in retarding the oxidation and deterioration of vulcanized rubber. It may well be that the presence of water during the heating with swelling agents as normally practiced in reclaiming operations has a significant influence in retarding deterioration by oxidation. Possibly the almost universal use of steam as the heating medium in reclaiming has advantages beyond that of supplying thermal energy economically.

F. S. Rostler and R. M. White<sup>21</sup>, noting the higher swelling increments of unsaturated oils as compared to saturated, suggested that this may be related

to reaction between the former and sulfur of vulcanization, such as may occur at reclaiming temperatures.

*Tackifiers and lubricants.*—These include a wide range of mineral oils, resins, etc., their function being to improve the workability of the resultant stock during the milling operation which follows heating, and to improve the characteristics of the ultimate reclaim. They are regarded as contributing little to molecular disaggregation, but function as useful tools in the "tailor making" of reclaims, since it is sometimes possible to use substantially higher ratios of these oils, etc., thereby reducing thermal treatment with resulting modification of the properties of the reclaim. The reclaiming of mixed polymers can be facilitated by the addition of swelling agents, etc., which have roughly the same effect on the various polymers.

*Reclaiming agents.*—While these are of particular application to GR-S and nitrile rubbers, they have some usefulness in the reclaiming of natural scrap. Several interesting and important publications are available on this subject<sup>22,23,24,25</sup>. A wide range of products has been prepared including the reaction products of monoaryl hydrazines with aldehydes and ketones, long chain aliphatic amines, cyclohexylamine and the diaryl sulfides<sup>26</sup>. Another important class is that of the Renacits, i.e., naphthyl, trichlorophenyl, and 9-anthranyl mercaptans. Certain of these bodies are found effective in alkali reclaiming, whereas others are only useful in neutral processes. The mechanism of these reclaiming agents is as yet a subject open to further research, but there are strong reasons for believing that they catalyze peroxidative chain scission and suppress or inhibit oxidative aggregation reactions.

J. C. Amberlang and G. E. P. Smith<sup>24</sup> suggested that polyalkyl sulfides may react and disrupt the network structure by combining with the sulfur of the crosslinks. Direct oxygen determinations prove that 4,6-di-*tert*-butyl-*m*-cresol sulfide is an oxidative catalyst for many types of cured GR-S. The development of agents and techniques such as will admit of reclaiming by attacking the crosslinks rather than by extensive chain scission may well point the way to superior quality reclaims.

*Reclaiming synthetic rubbers.*—As compared with natural scrap, there are strong tendencies towards progressive hardening at the temperatures normally used for fabric destruction, but the difficulties have been overcome to a great extent. A much finer degree of disintegration is necessary, together with increased ratios of suitable swelling agents and, most important, the presence of reclaiming aids.

D. S. LeBeau<sup>27</sup> discusses the effect of polymer structure upon the course of the reclaiming reaction explaining that in the case of GR-S, peroxidative chain scission is much less favorable than with natural rubber, while re-aggregation reactions are much more prone to occur. It has been suggested, and to some extent proved, that suitable reclaiming agents tend to correct these undesirable features, and in addition may further enhance plasticization by the destruction of crosslinks. The reclaiming of mixed GR-S and natural rubber requires a suitable choice of swelling agents, period and temperature of heating, etc., in order to avoid the oversoftening of the natural rubber and at the same time plasticize the GR-S to a sufficient degree. Vulcanized GR-S at reclaiming temperatures initially shows considerable softening, quickly followed by hardening, but by suspending the heat treatment prior to hardening setting in, successful reclamation of GR-S can be achieved. This is the basis of the Dip Process<sup>28</sup>.

*Butyl rubber.*—Reference has already been made to this subject. The rubber is very readily plasticized by heat and shows no tendencies for rehardening. Plasticization would appear to be linked up with the destruction of crosslinks, together with the absence of re-aggregation tendencies.

*Neoprene and nitrile rubbers.*—The heat hardening of these is more pronounced than with GR-S with consequent reclaiming difficulties. These rubbers are not, as yet, extensively reclaimed. Success would appear to depend upon repression of re-aggregation reactions, and in this respect certain long chain aliphatic amines have been found effective. It is obvious that effective and economic reclaiming processes for these types of synthetic rubbers are likely to be of increasing importance as the uses of these polymers are extended.

*Silicone rubbers.*—Little work has been done on this subject, but vulcanized products have been plasticized successfully by mechanical working and by heating in high pressure steam<sup>29</sup>.

*Mechanical working.*—Completion of the reclaiming process involves very severe mechanical working by milling, straining and passage through the close set refining mills. While the latter operations are primarily designed to remove extraneous matter and to achieve the necessary level of homogeneity, they also induce certain deep seated changes in the structure of the rubber molecules themselves.

H. F. Palmer and F. L. Kilbourne, Jr.<sup>9</sup> have investigated these in some detail. Milling and straining do not appear to increase either acetone or chloroform extracts to any significant extent, but refining was found to increase the latter. It is interesting to note that where there is a wide difference between refiner roll temperatures (in actual example quoted 132° and 118° C against 49° and 63°, and 138° and 136° against 77° and 82° C) the cooler refiner rolls lead to greater increases in chloroform extract than do the hotter rolls.

A recent paper by M. Pike and W. F. Webster<sup>30</sup> on the subject of mastication of rubber at various temperatures and conditions, indicates that at lower temperatures mechanical rupture of bonds takes place, followed by stabilization by oxygen or other suitable means and it may well be that the increase of chloroform extract under very low temperature refining conditions arises from a somewhat similar mechanism.

Most practical reclaimers are aware of the marked difference resulting from hot and cold milling and refining. The Dunlop Rubber Company<sup>31</sup> have patented a process of reclaiming by grinding cured rubber with pine oil on rolls below 60° C and raising the temperature to 60° to 120° C when a coherent sheet is formed. Milling at such temperatures would indicate the possibility of breakdown beyond that obtained at the more usual working temperatures. From a more practical angle, it is important to ensure that the thermal treatment of the waste is sufficient to promote the necessary degree of smoothness of texture in the ultimate reclaim. If the material presented to the mills is unduly soft or tacky the refiner rolls are unable to perform their function of eliminating the hard nibs. Excessive plasticity will reduce the desired shearing effect, and likewise slow down production and prejudice quality.

F. L. Kilbourne Jr.<sup>32</sup>, in a comprehensive paper on the reclaiming of synthetic rubber suggests that waste after devulcanization consists of fragmentary molecules which during refining and straining are converted to oxidized fragmentary molecules. Inadequate devulcanization is stated to increase the tendency to oxidation. It is thought that with progressive devulcanization the active centers lose some activity and in consequence a thorough heat treatment

reduces storage hardening by decreasing the formation of oxygen bridges between the molecules.

### SUMMARY AND DISCUSSION

From this brief outline it will be seen that the mechanism of devulcanization is, as yet, imperfectly understood, but some fundamental and practical progress has been achieved. Complete understanding cannot be attained without a better knowledge of the structure of vulcanized rubber and other polymers. The work of D. S. LeBeau, F. L. Kilbourne and others has established that hydroperoxidative chain scission is predominant in reclaiming and that secondary oxidation is small and incidental. The relative ease with which natural rubber responds to breakdown as compared with GR-S, nitrile rubbers, neoprene, etc., indicates the necessity of research to devise other means of inducing plasticization in the latter. If, as one may assume, the properties of vulcanizates are largely induced by crosslinking, the removal or modification of these is the obvious way to approach the problem. It has already been indicated that there is some reason to believe that certain of the reclaiming aids function in this way. The authors hold the view that modifications in the nature of the combination of sulfur and other crosslinking agents may well play a significant role in the plasticization which can be induced by heat in both natural rubber and GR-S. There is ample evidence that reclaiming temperatures will induce far reaching modifications in the degree of crosslinkages, etc., and this may contribute materially to the devulcanization process. The prospects of basically improving reclaim are severely limited so long as the methods employed rely upon chain scission resulting in fragmentary molecules, and it is felt that attention might profitably be paid to the problem of removing or suitably modifying crosslinkages to diminish the vulcanized characteristics which they confer, or alternatively to carry the breakdown almost as far as the monomer and follow this with repolymerization.

While a definite minimum of thermal treatment is as yet necessary for practical reclaiming, it is accompanied by a certain amount of degradation. H. F. Palmer and F. L. Kilbourne<sup>9</sup> compared reclaim prepared by two methods: (a) high plasticization and moderate heat treatment (i.e., low chloroform extract) and (b) moderate plasticization and severe heat treatment (i.e., high chloroform extract). Type (b) can be considered to have suffered much more extensive molecular breakdown than (a). The two reclaims were compared in a standard formula and in spite of the high oil content, the cured characteristics of the former were somewhat superior to (b). This finding would suggest that chloroform extract makes but limited contribution to ultimate physical properties, though it is important since it contributes to the plasticity of the uncured reclaim. This finding confirms that the achievement of the necessary plasticity by means of a smaller extent of thermal treatment, i.e., reduced molecular disaggregation, suggests another approach to improving reclaim qualities. Since a very high proportion of waste contains fabric and high temperatures are required to remove it, the practical solution of the problem is still some distance away. The nearest approach perhaps lies in the mechanical removal of fabric to obtain clean vulcanized waste.

In the meantime, we are now beginning to obtain some real understanding of the mechanism of orthodox reclaiming, an essential prerequisite for improving existing processes and developing new means of handling synthetics.

If molecular disaggregation is solely responsible for reclaiming and the fate

of the crosslinkages is entirely negative, the chloroform extract should within limits be a positive index of efficiency and workability. This is not the case and other changes must be considered. As pointed out, the greater proportion of the combined sulfur of the original waste is retained in the chloroform insoluble fraction, and it is felt that a study of the mode of combination of the sulfur, i.e., inter- or intramolecular, etc., would be illuminating. As stated earlier, the residual elasticity of all reclaims indicates that some of the original condition of vulcanization is retained, and it may well be that this insoluble fraction retains much of its sulfur combined in an intramolecular form which would partially account for its comparative inability to resist deformation. On the other hand, while oxidation is considered to be mainly incidental to the process of hydroperoxidative chain scission taking place during heating, it may play a more significant role during the milling process. To a certain extent we may draw an analogy between the mill plasticization of the chloroform insoluble rubber and the mastication of unvulcanized rubber. It is probable that the chloroform soluble rubber serves as a very efficient plasticizer for the insoluble and that one of the functions of mechanical working is to effect the dispersion of the two. The relatively small increase in chloroform extract which results from straining and refining makes clear that we cannot regard this as mere extension of the prior heat treatment.

#### CONCLUSION

Much of the foregoing is indeed speculative and, until such time as the process of vulcanization is fully understood, this state of affairs will remain. The methods of trial and error upon which the reclaiming industry was originally founded will not be so successful with the synthetic rubbers as they were with the natural product, and a better understanding of existing processes is essential for the development of procedures.

#### SUMMARY

The general principles of rubber reclaiming have been briefly described. References have been made to some of the more recent work on this subject, and some of the common ground of reversion and reclaiming has been indicated. Some speculation on the possibilities of further basic improvements has been put forward.

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# ORGANIC SULFIDES AND POLYSULFIDES. I. DESULFURIZATION REACTIONS \*

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## INTRODUCTION

Polysulfides, polysulfide types of synthetic rubbers (Thiokol Type A, etc.) and vulcanization accelerators (thiazoles, thiurams, etc.) are used in the rubber industries. These materials have uncertain structures, reactions and identifications. Even simple polysulfides, such as tri- or tetrasulfides, have until now not been obtained in pure form, and we have only assumed the existence of them from the use of simple analytical methods. The polysulfide polymers are prepared by the reaction of sodium polysulfide and organic dichloride, but their structures are uncertain. The results of reactions between the organic polysulfides and mercury, copper, potassium cyanide (sodium cyanide) and sodium sulfite will be discussed here.

## PREPARATION OF MATERIALS

*p,p'-Ditoly sulfide*<sup>1</sup>.—*p*-Toluidine was dissolved in hydrochloric acid, and solution of sodium nitrite was added to the solution, with cooling, to form the diazonium chloride. The product treated with sodium sulfide solution, vacuum distilled (b.p. 175°/16 mm Hg), and then recrystallized from alcohol gave crystalline needles, melting at 57° C. The analyses of this and of other sulides are given in Table I.

*p,p'-Ditoly disulfide*<sup>2</sup>.—Thio-*p*-cresol (m.p. 43°) was dissolved in acetic acid and after adding FeCl<sub>3</sub> the solution reacted on heating. Recrystallization from alcohol gave crystalline needles melting at 46°.

*p,p'-Ditoly trisulfide*<sup>3</sup>.—An ether solution of sulfur dichloride was added to a solution of thio-*p*-cresol in ether with cooling. Recrystallization of the product from alcohol or ether gave a light yellow crystalline solid, m.p. 76° C.

*p,p'-Ditoly tetrasulfide*<sup>4</sup>.—An ether solution of sulfur monochloride was added to an ether solution of thio-*p*-cresol with cooling. Recrystallization of the product from alcohol or ether gave a yellow crystalline product.

*Dibenzyl sulfide*<sup>5</sup>.—Benzylchloride (b.p. 174–180°C), dissolved in alcohol, was heated to about 60° C. A solution of sodium sulfide was added dropwise. An oily material separated on cooling. Recrystallization from alcohol gave a solid, m.p. 48.5°.

*Dibenzyl disulfide*<sup>6</sup>.—Sodium disulfide solution was prepared by adding the calculated quantity of sulfur to a solution of sodium sulfide. A reaction was then carried out as in the case of dibenzyl sulfide. Oily material was obtained which crystallized from alcohol, m.p. 70.5° C.

\* Translated from the *Journal of the Society of the Rubber Industry of Japan*, Vol. 23, pages 212–215 (1950). This and the following five translations were supplied through the courtesy of E. M. Fettes and the Thiokol Chemical Corporation.

*Dibenzyl trisulfide*<sup>7</sup>.—Benzyl mercaptan (b.p. 76°/12 mm Hg, 82.5°/13 mm Hg), prepared from benzyl chloride and sodium hydrosulfide reacted with sulfur dichloride in ether solution. The product was recrystallized from carbon tetrachloride, yielding crystalline needles, m.p. 49°.

*Dibenzyl tetrasulfide*<sup>8</sup>.—Benzyl mercaptan was reacted with sulfur chloride in an ether solution. Recrystallization of the product from ether or carbon tetrachloride gave a yellowish crystalline material, m.p. 54° C.

*Thiodiglycolic acid*<sup>9</sup>.—Sodium salt, obtained by adding sodium hydroxide to a solution of monochloroacetic acid, was treated with sodium sulfide at 80° C. After cooling, the solution was acidified by sulfuric acid and then extracted with ether. Thioglycolic acid was obtained from the ether extract. The product was recrystallized from ether or warm water, m.p. 128–129° C.

*Dithiodiglycolic acid*<sup>10</sup>.—The sodium salt of monochloroacetic acid was reacted with sodium disulfide in solution as above, and then acidified with sul-

TABLE I  
ELEMENTARY ANALYSES

Sulfides	M.P. (° C)	C, %		H, %	
		Obs.	Cal.	Obs.	Cal.
<i>p,p'-Ditolyl</i>					
mono-	57	78.71	78.50	6.67	6.54
di-	46	68.41	68.29	5.72	5.69
tri-	76–77	60.20	60.43	5.31	5.04
tetra-	75	54.58	54.20	4.66	4.52
<i>Dibenzyl</i>					
mono-	48.5	78.55	78.50	5.92	6.54
di-	70.5	68.66	68.29	5.17	5.69
tri-	49	60.84	60.43	6.13	5.04
tetra-	54	53.04	54.20	5.37	4.52
<i>Diglycolic acid</i>					
mono-	128–129	32.11	32.00	4.28	4.00
di-	100	27.20	26.37	3.64	3.29
tri-	123–124	22.84	22.43	3.02	2.80
tetra-	112–113	20.12	19.51	2.57	2.44

furic acid and extracted with ether. Recrystallization from ether gave a solid, m.p. 100°.

*Trithiodiglycolic acid*<sup>11</sup>.—Thioglycolic acid ( $\text{HSCH}_2\text{COOH}$ ) obtained from the reaction between monochloroacetic acid and sodium hydrosulfide was treated with sulfur dichloride in ether solution. Recrystallization of the product from ether gave a solid melting at 123–124°.

*Tetrathiodiglycolic acid*.—Thioglycolic acid was treated with sulfur monochloride in ether solution and the product recrystallized from ether, m.p. 112–113° C. However, the product decomposes, even at room temperature.

The reactions of mercury, copper, potassium cyanide or sodium sulfite with the sulfides to form  $\text{HgS}$ ,  $\text{CuS}$ ,  $\text{KCNS}$  and  $\text{Na}_2\text{S}_2\text{O}_3$  were studied. These reagents do not react with mercaptans.

*Reactions with mercury*.—Each powdered *p,p'-ditolyl* mono-, di-, tri and tetrasulfide was added to mercury at room temperature. The tetrasulfide reacted with mercury gradually and gave black mercury sulfide. Each product

extracted by ether and recrystallized from alcohol had melting points as follows:

	-S <sub>1</sub> -	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -
M.p. Before reaction	57° C	46	76-77	75
After reaction	57	46	46	45-46

From these results it is apparent that only the tri- and tetrasulfides were desulfurized by mercury to form disulfide by losing one and two atoms of sulfur, respectively. Mono- and disulfides did not react even on warming on the water bath. Desulfurization of the tri- and tetrasulfides was accelerated by heating.

Benzyl tri- and tetrasulfides, in similar experiments, gave mercury sulfide and their reaction velocities were faster than in the ditolyl series. Tetrasulfide reacted more readily than sulfur and gave mercury sulfide. Results were as follows:

	-S <sub>1</sub> -	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -
M.p. Before reaction	49	71	49	54
After reaction	49	71	70-71	71

The mono- and disulfides did not react even on heating. On the other hand, tri- and tetra-sulfides gave disulfides, by desulfurization.

In the cases of diglycolic acid, the di-, tri- and tetrasulfides gave mercury sulfides, and they reacted more readily than the dibenzyl series, the results being indicated as follows:

	-S <sub>1</sub> -	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -
M.p. Before reaction	128-129	100	123-124	112-113
After reaction	128-129	126-128	127-129	128-129

The di-, tri- and tetrasulfides were converted to monosulfide by heating, but the monosulfide was unchanged.

The relative reaction velocity of desulfurization by mercury of the various series of sulfides is *p,p'*-tolyl < dibenzyl < diglycolic acid series. The first two gave disulfides on reaction, but the diglycolic acid series gave monosulfides. The higher the content of sulfur in a polysulfide, the easier the desulfurization is carried out.

*Reactions with copper.*—Treating with powdered copper, the results were the same as in the cases of mercury. *p,p'*-Tolyl and dibenzyl series gave disulfides, and diglycolic acid series gave monosulfides. Cupric sulfide was obtained and the reaction velocity is slower than for that with mercury.

*Reactions with potassium cyanide.*—Each sulfide was dissolved in alcohol or acetone, added to a solution of potassium cyanide and then heated on a water bath. After extracting with ether, the product was recrystallized from alcohol and the melting point measured. *p,p'*-Tolyl and dibenzyl series, as with the mercury and copper, gave disulfide. Mono- and disulfides gave no reaction.

	-S <sub>1</sub> -	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -
<i>p,p'</i> -Ditolyl series	57	46	46	46
Dibenzyl series	49	70-71	70-71	70-71

The sulfides of diglycolic acids dissolved in water reacted with ferric chloride. Di-, tri- and tetrasulfides showed the formation of SCN- ion; on the other hand, the monosulfide gave no reaction. Reacting with potassium cyanide, di-, tri- and tetrasulfides were converted to monosulfide by desulfurization, but the

product was not pure monosulfide. The ease of desulfurization, in this case, is *p,p'*-tolyl < dibenzyl < diglycol.

*Reactions with sodium sulfite ( $Na_2SO_3$ ).*—A saturated solution of sodium sulfite was added to an acetone solution, in which each sulfide had been dissolved, and then the mixture was heated. After extraction and recrystallization, the melting point of the product was measured. In the cases of *p,p'*-tolyl and dibenzyl series, tri- and tetrasulfides were changed to disulfide; on the other hand, mono- and disulfides were not changed.

The sulfides of diglycolic acid series were dissolved in water and a saturated solution of sodium sulfite added. In these cases, di-, tri- and tetrasulfides reacted, and sodium thiosulfate was identified by the silver nitrate method. Monosulfide did not react. According to these results, di-, tri- and tetrasulfides were desulfurized by sodium sulfite. However we could not get pure monosulfide from the products.

#### CONCLUSIONS

Mercury, copper, potassium cyanide and sodium sulfite were found to desulfurize organic polysulfides. In the *p,p'*-ditolyl and in the dibenzyl series, the di-, tri- and tetrasulfides gave disulfide by desulfurization. On the other hand, in the case of diglycolic acids, di-, tri- and tetrasulfides gave monosulfides. The sulfide, which has high polarity in its radical, is easily desulfurized. The relative ease of desulfurization is—diglycolic acid > dibenzyl > *p,p'*-tolyl. In the same series, the higher the sulfur content, the more unstable it seems to be. Mercury is more reactive with sulfides than is copper.

#### ACKNOWLEDGMENTS

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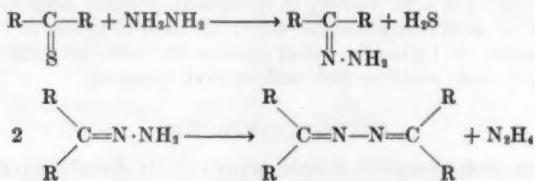
## ORGANIC SULFIDES AND POLYSULFIDES. II. REACTIONS WITH HYDRAZINE, ETHYLEDIENEDIAMINE AND AMMONIA \*

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In the preceding paper<sup>1</sup>, the synthesis and the reactions of organic sulfides and polysulfides with mercury, copper, cyanides and sodium sulfite were discussed. In this present paper, reaction of these sulfides with distilled hydrazine hydrate ( $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ , b.p. 119–120°), (distilled) ethylenediamine (b.p. 117°), and ammonia will be discussed. *p*-Tolyl mercaptan, m.p. 43°, and benzyl mercaptan, b.p. 76°/12 mm or 82.5°/13 mm, are also included in this study.

*Reactions of organic polysulfides with hydrazine hydrate.*—Hydrazine hydrate gives a ketazine bond by reaction with a thioketone:



If a sulfur atom is adjacent to a sulfur bond such as  $-\text{S}-$ ,  $-\overset{\text{S}}{\underset{\parallel}{\text{S}}}-$ , and  $-\overset{\text{S}}{\underset{\parallel}{\text{S}}}-\text{S}-$ , the sulfur of the side chain will react with the thioketone and give a ketazine bond.

Each sulfide was dissolved in alcohol and then hydrazine hydrate was added to the solution. Mono-, di-, tri- and tetrasulfides of the tolyl series, and tolyl mercaptan reacted gradually with hydrazine in the alcohol solution at room temperature. Mercaptan, and tri- and tetrasulfides gave yellow to brown solutions. In these cases tri- and tetrasulfides generated hydrogen sulfide which was identified with lead acetate. After concentrating the reaction solutions and standing, crystals formed and were recrystallized from alcohol. Melting point data were as follows:

	<i>p</i> -Tolyl	-SH	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -	-S <sub>4</sub> -
M.p.	Before reaction	43° C	57° C	46° C	77° C	75° C
	After reaction	46° C	57° C	46° C	46° C	46° C (H <sub>2</sub> S)

Mercaptan was oxidized to give disulfide, while tri- and tetrasulfide also gave disulfide.

\* Translated from *Journal of the Society of the Rubber Industry of Japan*, Vol. 24, pages 263–265 (1951).

When sulfur was dissolved in hydrazine hydrate, ammonia and hydrogen sulfide were generated. However, we could not obtain the crystalline form of  $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{S}$  by decomposition with water<sup>3,4</sup>. The sulfur removable from tri- and tetrasulfides thus reacts as does free sulfur.

Benzyl mercaptan and benzyl mono-, di-, tri- and tetrasulfides were treated with hydrazine, and the products obtained were identified by elemental analysis and by melting point. Melting point data were as follows:

	Benzyl	-SH	-S <sub>1</sub> -	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -
M.p. Before reaction		liquid (b.p. 76°/12 mm Hg)	49	71	49	54
After reaction		71	49	71	71	(H <sub>2</sub> S)

Mono- and disulfides gave no reaction; on the other hand, tri- and tetrasulfides were desulfurized and converted to disulfide. Benzyl mercaptan was oxidized to disulfide.

Thiodiglycolic acid and dithioglycolic acid were treated with hydrazine in water solution. At room temperature, thiodiglycolic acid gave resinous material without the generation of hydrogen sulfide. This resinous material could not be identified. In case of reaction with heating, hydrogen sulfide was found and lead sulfide was precipitated by treatment with lead acetate. Dithioglycolic acid was treated with hydrazine at room temperature. It is assumed that dithioglycolic acid was desulfurized by hydrazine.

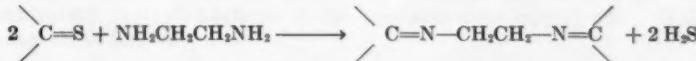
From these results, we found that tri- and tetrasulfides of both the *p*-tolyl and benzyl series were desulfurized to disulfide by hydrazine, and mercaptan was oxidized to disulfide. All the polysulfides of the diglycolic acid series were desulfurized to monosulfide at room temperature.

*Reaction of polysulfides and ethylene diamine.*—Ethylenediamine was added to alcoholic solutions of the polysulfides. On heating on a water bath, tri- and tetrasulfides and mercaptan reacted and on standing crystals came down. The melting points of the products after reaction were as follows:

	-SH	-S <sub>1</sub> -	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -
M.p. Tolyl series:	46° C	57	46	46	46
Benzyl series:	71	49	71	71	71

Mercaptans were oxidized, and disulfides gave no change. Tri- and tetrasulfides were desulfurized to disulfide.

Thioglycolic acid gave resinous materials, and hydrogen sulfide was evolved on heating. On the other hand, dithioglycolic acid also showed the generation of hydrogen sulfide. Qualitatively, hydrazine was more reactive than ethylenediamine. The reaction between ethylenediamine and a thioketone has been reported<sup>5</sup> to be:



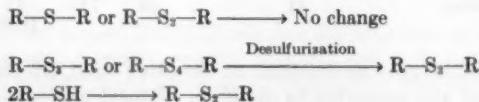
*Reaction of polysulfides and ammonia.*—Ammonia was added to alcoholic solutions of the organic polysulfides. By heating on a water bath and then cooling, crystalline products were obtained. After recrystallization from alcohol, melting points were measured. In the case of the tolyl and benzyl

series, tri- and tetrasulfides were converted to disulfides. Mercaptans also gave disulfides. Mono- and disulfides were unchanged.

Dithioglycolic acid was desulfurized by ammonia and thioglycolic acid generated hydrogen sulfide in the presence of ammonia by heating. Thioke-tone groups give ketones by reaction with ammonia<sup>6</sup>.

### CONCLUSIONS

The results showed that desulfurization occurred in the reaction between organic polysulfides and hydrazine, ethylenediamine or ammonia. Hydrazine, ethylenediamine and ammonia react with organic sulfides as follows:



In the case of strong polarity, even the glycolic acid series which has di-sulfide groups was desulfurized to monosulfide. The stronger the polarity of the molecule, the easier it is to desulfurize. The reaction of polysulfides can be distinguished from the reaction of thioketones.

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## ORGANIC SULFIDES AND POLYSULFIDES. III. REACTIONS WITH AMINES \*

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In the previous paper<sup>1</sup>, the reactions of organic polysulfides with hydrazine, ethylenediamine and ammonia were reported. Now, in this paper, reactions between organic polysulfides with such amines as monomethylamine, dimethylamine, trimethylamine, aniline and diphenylamine will be discussed. The results obtained will give a new answer to the questions such as peptization and vulcanization.

Monomethylamine (b.p. -6°), dimethylamine (b.p. 8°) and trimethylamine (b.p. -3°) were prepared from their hydrochlorides by adding sodium hydroxide and absorbing them in alcohol, which was cooled in an ice bath. These alcoholic solutions were used. Aniline (b.p. 184°) and diphenylamine (m.p. 54°) were commercial samples. The sulfides used were described in the previous paper.

### REACTIONS WITH ALIPHATIC AMINES

*Reactions with momomethylamine.*—Benzyl mercaptan, as well as benzyl mono-, di-, tri- and tetrasulfides did not react with momomethylamine at room temperature. However, the mercaptan and the tri- and tetrasulfides reacted on heating, and after concentrating the solutions, crystalline products were obtained. From the melting points and elemental analyses, it can be seen that mercaptan, tri- and tetrasulfides were converted to disulfides; on the other hand, the mono- and disulfides were unchanged. With respect to rate of conversion to disulfide, mercaptan is fastest, and then the tetra- and trisulfide. The tri-sulfide is the slowest. The melting points before and after reaction were as follows:

	Benzyl	-SH	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -	-S <sub>5</sub> -
M.p.	Before reaction	liquid	49	71	49	54
	After reaction	71	49	71	70-71	71

The reaction mechanisms are believed to be the same as in the case of ammonia.

*p*-Tolyl mercaptan, *p,p'*-tolylmono-, di-, tri- and tetrasulfide were found to react with monomethylamine. The mercaptan, tri- and tetrasulfides were converted to disulfide, but the mono- and disulfides did not change. After concentrating, recrystallizations of the products were carried out. Melting points were as follows:

	<i>p</i> -Tolyl	-SH	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -	-S <sub>5</sub> -
M.p.	Before reaction	43	57	46	76-77	75
	After reaction	46	57	46	46	45-46

\* Translated from *J. Soc. Rubber Ind. Japan* 24, 266-268 (1951).

The desulfurization of *p*-tolyl tri- and tetrasulfides was faster than in the benzyl series. The mercaptan was the fastest, the trisulfide the slowest.

In the case of reactions of methylamine with thioglycolic acid and dithioglycolic acid, dithioglycolic acid was converted immediately and gave monosulfide and thioglycolic acid was changed to a brown solution. From these results it is believed that the reactions of polysulfides and methylamine were the same as those for ammonia.

*Reactions with dimethylamine.*—An alcoholic solution of dimethylamine was added to the sulfides and polysulfides. Generally speaking, the reaction velocities are faster than with monomethylamine. After recrystallization of the products, melting points were measured. The results were similar to those for methylamine, that is, in the tolyl and benzyl series, mercaptan tri- and tetrasulfides gave disulfide, and in the case of the glycolic acid series the mercaptan and dithioglycolic acid gave monosulfide.

*Reactions with trimethylamine.*—Reactions were carried out by heating. Results were similar to those with mono- and dimethylamine already mentioned. After reaction, melting points were determined and elemental analyses carried out. In the benzyl and tolyl series, mercaptan and tri- and tetrasulfides were changed to disulfide. Mono- and disulfides were not changed. In the glycolic acid series, even the dithioglycolic acid gave monosulfide.

From these results it is evident that mono-, di-, and trimethylamine gave the same reactions with organic sulfides and polysulfides, that is, mercaptan and tri- and tetrasulfides were changed to disulfides in the tolyl and benzyl series. On the other hand, in the glycolic acid series, disulfide also was changed to monosulfide. This is due to the lability of sulfur adjacent to a polar radical. The desulfurization reaction occurs easily with molecules having polar radicals. The relative facility of desulfurization is: glycolic acid > benzyl > tolyl. Tetrasulfides were easily desulfurized.

The relative reactivity of amines is  $(CH_3)_2N < CH_3NH_2 < (CH_3)_2NH$ . It is identical to the relative order of alkalinity of the amines. Considering only I-effect, the relative basicity must be  $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$ , but the nitrogen atom of  $(CH_3)_3N$  has three methyl groups; therefore, the basicity of trimethylamine is reduced by its back side strain. The actual basicity of the amines thus becomes  $NH_3 < (CH_3)_2N < (CH_3)NH_2 < (CH_3)_2NH$ .

#### REACTIONS WITH AROMATIC AMINES

*Reactions with aniline.*—Aniline was added to alcoholic solutions of the sulfides, and then the mixtures were heated for a long time. After six hours of heating, aniline separated on adding water. Hydrochloric acid was added to the mixture and the aniline thus dissolved in the water layer. The oily product was recrystallized from alcohol and its melting point measured. The results were:

	Benzyl	-SH	-S <sub>1</sub> -	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -
M.p.	Before reaction	liquid	49	71	49	54
	After reaction	liquid	49	71	49	53-54

It is evident that none of the sulfur compounds reacted.

*p*-Tolyl mercaptan, *p,p'*-tolyl mono-, di-, tri- and tetrasulfides were dissolved in alcohol and heated with aniline. Melting points after recrystalliza-

tion were as follows:

	<i>p</i> -Tolyl	-SH	-S <sub>1</sub> -	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -
M.p.	Before reaction	43	57	46	76-77	75
	After reaction	43	56-57	46	76	74-75

As in the benzyl series none of the *p*-tolyl sulfides reacted.

Sulfides of the glycolic acid series also gave no reactions. After reaction, water was added to remove aniline as an oily material. After concentrating the water layer, the product was recrystallized from alcohol. The melting points were:

	Glycolic acid	-S <sub>1</sub> -	-S <sub>2</sub> -
M.p.	Before reaction	128-129	100
	After reaction	127-129	100

*Reaction with diphenylamine.*—As with aniline, diphenylamine was heated with alcoholic solutions of sulfides for longer than ten hours. However, we could find no reaction. This is because of the still weaker basicity of diphenylamine. We did not carry out an experiment with triphenylamine. Triphenylamine, we suppose, will not react with organic sulfides.

Unlike aliphatic amines, aniline has a large resonance effect in its structure. Its ionization constant is  $3.8 \times 10^{-10}$  and this shows that aniline is a very weak base (aliphatic amines:  $10^{-3}$  to  $10^{-5}$ ). Aromatic amines, such as aniline and diphenylamine, do not react with organic polysulfides because of their weak basicity.

### CONCLUSIONS

1. Mono-, di-, and trimethylamine when treated with benzyl and tolyl mercaptan give disulfides; on the other hand, thioglycolic acid gives the monosulfide.
2. Aniline and diphenylamine do not react with mercaptans or organic sulfides.
3. Mono-, di- and trimethylamine react with organic polysulfides. The tri- and tetrasulfides of the tolyl and benzyl series give disulfides by desulfurization. The glycolic acid sulfides are desulfurized to monosulfide.
4. The relative desulfurization activities of mono-, di- and trimethylamine are  $(CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$ . This order is the same as for the basicity of these amines. Aromatic amines, because of their weak basicity, do not react with organic polysulfides.
5. The relative ease of desulfurization is in the order glycolic acid > benzyl > tolyl. The more sulfur a polysulfide contains, the more readily it desulfurizes. The mercaptan to disulfide reaction rate is faster than desulfurization of polysulfides.

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## ORGANIC SULFIDES AND POLYSULFIDES. IV. REACTIONS WITH DOCTOR SOLUTION, SILVER NITRATE, CUPRIC ACETATE AND LEAD ACETATE \*

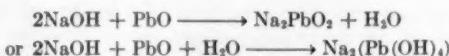
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In previous papers<sup>1,2,3</sup> the properties and reactivities of the organic sulfides and polysulfides have been discussed. In this paper the author discusses the reactions between organic polysulfides and reagents which react with the mercaptan radical ( $-SH$ ). Doctor solution, silver nitrate, lead acetate and cupric acetate will be discussed here.

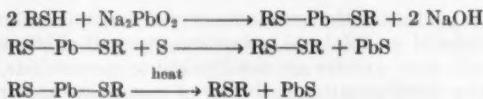
*Preparation of materials and reagents.*—The sulfides and polysulfides used were the same as those used in previous papers<sup>1,2,3</sup>.

Doctor solution is customarily made by mixing sodium hydroxide with lead oxide or lead hydroxide<sup>4</sup>; the author saturated a 20–25% sodium hydroxide solution with lead oxide. These reactions are supposed to be as follows<sup>5</sup>:

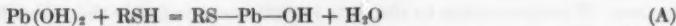


This formula is equivalent to  $\text{Na}_2\text{PbO}_2$  with two molecules of water of hydration.

*Doctor solution reactions.*—Doctor solution reacts with organic polysulfides as follows:



In such cases,  $\text{RS—Pb—SR}$  and  $\text{PbS}$  can be determined. The reaction of doctor solution has been presented by Ott and Reid<sup>6</sup> to involve hydration in the presence of alkali of  $\text{PbO}$  to  $\text{Pb}(\text{OH})_2$  which reacts with mercaptan as follows:



They surmised that (A) and (B) are the chief reactions and that (E) is possible but is not important in the case of a secondary mercaptan. The reaction of

\* Translated from *J. Soc. Rubber Ind. Japan* 28, 141–145 (1955).

mercaptan doctor solution in any case is one of producing RS—Pb—SR and PbS.

Doctor solution was added to alcoholic solutions of mercaptan or organic sulfides. Benzyl mercaptan and benzyl di-, tri- and tetrasulfide reacted with doctor solution and gave a precipitate of lead sulfide. Mercaptan is most sensitive in this reaction. The reaction velocity was accelerated by heating. The sulfides thus reacted with doctor solution in the presence of alkali. Only benzyl monosulfide failed to react. The doctor solution reactions involve

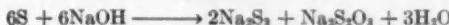


that is, mercaptan and a sulfenic acid can be produced<sup>7</sup>. The reaction velocity of mercaptan is fastest, and then tetra-, tri-, and disulfide. All give lead sulfide except monosulfide which does not give any reaction.

*p*-Tolyl mercaptan and *p,p'*-ditolyl mono-, di-, tri- and tetrasulfides were treated with doctor solution. They showed the same reactions as in the case of the benzyl series. The reaction velocities of di-, tri- and tetrasulfide, except mercaptan, were slower than in the benzyl series. Monosulfide gave no reaction.

In cases of thioglycolic acid ( $\text{HOOCCH}_2\text{—S—CH}_2\text{COOH}$ ) and dithioglycolic acid ( $\text{HOOCCH}_2\text{—SS—CH}_2\text{COOH}$ ), the former gave a white precipitate and the latter a reddish brown one. Both changed to black on standing. The black precipitate was identified as lead sulfide but the composition of the initial precipitates was uncertain.

Sulfur reacted with doctor solution on heating and gave lead sulfide. Sodium sulfide, formed from sodium hydroxide and sulfur:



reacted to precipitate lead sulfide. Therefore, in the reaction with doctor solution, the polysulfide, which is easily desulfurized, gives lead sulfide.

*Reaction of silver nitrate and organic sulfides.*—The reaction reported<sup>8</sup> in the qualitative analysis of mercaptans is as follows:



The authors dissolved the samples in alcohol and then added silver nitrate to the solution. Benzyl and *p*-tolyl mercaptan readily reacted with silver nitrate and gave mercaptide. However, the corresponding mono- and disulfides did not react. In the case of tri- and tetrasulfides, desulfurization occurred to form disulfide and silver sulfide. The formation of disulfides was verified by melting points and elemental analyses. The benzyl series was more reactive than the tolyl series and the tetrasulfide was desulfurized more easily than the trisulfide.

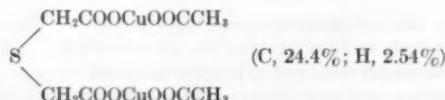
In the reactions of silver nitrate and the glycolic acid series, thioglycolic acid gave a white precipitate (found: C, 18.86%; H, 1.44%). It is believed to be  $\text{HOOCCH}_2\text{SCH}_2\text{COOAg}$  (calcd.: C, 18.65%; H, 1.94%). Dithiodiglycolic acid gave both a white and a black precipitate. The black precipitate was silver sulfide, but the composition of the white was uncertain. We conclude that dithiodiglycolic acid was desulfurized by silver nitrate.

*Reactions with lead acetate and cupric acetate.*—As we have discussed in the previous paper<sup>1</sup>, the organic polysulfides were easily desulfurized by copper or

mercury<sup>1</sup>. It has been found that cupric acetate and lead acetate, by dissociation to Cu<sup>++</sup> and Pb<sup>++</sup>, react with mercaptan and form mercaptide<sup>9</sup>.

Benzyl and *p*-tolyl mercaptan reacted easily with cupric acetate and lead acetate, and they gave mercaptides. On the other hand, mono-, di-, tri- and tetrasulfides of both the benzyl and tolyl series did not react with cupric acetate or with lead acetate in an alcoholic solution, even on heating. Recovered starting materials were identified by melting points and elemental determinations.

Thiodiglycolic acid reacted with cupric acetate to give a blue precipitate (found: C, 24.5%; H, 2.58%). Ash remained after ignition. This precipitate is believed to be



Dithiodiglycolic acid reacted with cupric acetate, but the product obtained could not be identified.

### CONCLUSIONS

1. In mixtures of doctor solution and benzyl and *p*-tolyl sulfides, di-, tri- and tetrasulfide reacted and formed lead sulfide, but monosulfide did not react.
2. In the case of thiodiglycolic acid and dithiodiglycolic acid, dithiodiglycolic acid gave lead sulfide.
3. Sulfur gave lead sulfide by reaction with doctor solution.
4. Mercaptide formed by the reaction between silver nitrate and mercaptan. Mono- and disulfide of the benzyl and tolyl series gave no reaction. Tri- and tetrasulfide showed desulfurization, and gave disulfide. Dithiodiglycolic acid reacted with silver nitrate and gave silver sulfide.
5. Lead acetate and cupric acetate reacted readily with mercaptan. Mono-, di-, tri- and tetrasulfides of the benzyl and tolyl series gave no reaction even on heating.
6. Mercaptan was most reactive in the reactions with doctor solution and with silver nitrate. The more sulfur the organic polysulfide contained, the more reactive it was. The relative order of reactivity in these series were: glycolic acid > benzyl > tolyl.

### ACKNOWLEDGMENT

The author wishes to thank Dr. H. Kambara for his helpful suggestions.

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## ORGANIC SULFIDES AND POLYSULFIDES. V. REACTIONS WITH METHYL IODIDE \*

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Trimethylsulfonium iodide ( $\text{CH}_3)_3\text{S}\text{I}$  is formed by the reaction between methyl iodide and organic monosulfide<sup>1</sup> and disulfide<sup>2,3</sup>. It is also formed by the action of methyl iodide on trithiomethylene (trimer of thioformaldehyde)<sup>4</sup>. However, nothing has been reported about the reaction between polysulfides and methyl iodide. Recently, M. L. Selker and A. R. Kemp<sup>5,6</sup> have reported the formation of trimethylsulfonium iodide from methyl iodide and one third (1/3) of the sulfur in hard rubber from natural rubber or GR-S. Also, they have studied the mechanism of vulcanization of rubber and the type of sulfur bonds formed.

Reactions between mono-, di-, tri- and tetrasulfides and also mercaptans with methyl iodide will be discussed in the present paper.

The organic sulfides and polysulfides which were studied have been described in a previous paper<sup>7</sup>. Methyl iodide was used after distillation.

*Reaction of benzyl mercaptan, benzyl mono-, di-, tri- and tetrasulfides with methyl iodide.*—Ten cc of methyl iodide was added to 1 g of each material and the mixture heated in a sealed tube for two hours at 100° C. Dark red products were obtained. Unreacted methyl iodide was removed under vacuum. The products were recrystallized from alcohol.

In the reaction between mono-, di-, tri- and tetrasulfide with methyl iodide, a colorless product, m.p. 203°, was obtained. This product was soluble in water and in alcohol, and it was identified as a halogen compound by the Beilstein test. Its elemental analysis was C 17.67%, H 4.50%. Therefore, it is trimethylsulfonium iodide (C 17.62%, H. 4.41%).

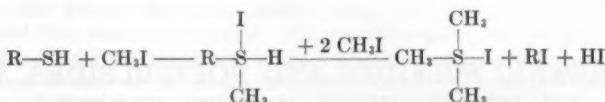
In the case of the reaction of benzyl mercaptan, the same results were obtained; the product had a melting point of 203°; it was soluble in both alcohol and water. However, in this case we had also another product which has a melting point of 71° C and was soluble in alcohol but not soluble in water. It was thought to be benzyl disulfide from its elemental determination and melting point.

	C %	H %
M.p. 203° C ( $\text{CH}_3)_3\text{S}\text{I}$ (calcd.)	17.37	5.11
	17.62	4.41
M.p. 71° C $\text{C}_6\text{H}_5-\text{S}-\text{S}-\text{C}_6\text{H}_5$ (calcd.)	68.21	5.54
	68.29	5.69

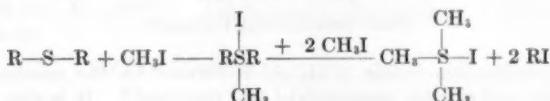
From these results, it is evident that mono-, di-, tri- and tetrasulfide and mercaptan in the benzyl series gives trimethyl sulfonium iodide on reaction with methyl iodide at 100° C.

\* Translated from *J. Soc. Rubber Ind. Japan* 28, 1-4 (1955).

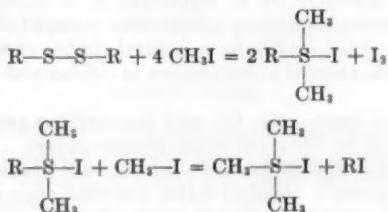
The reaction mechanism is set forth as follows:



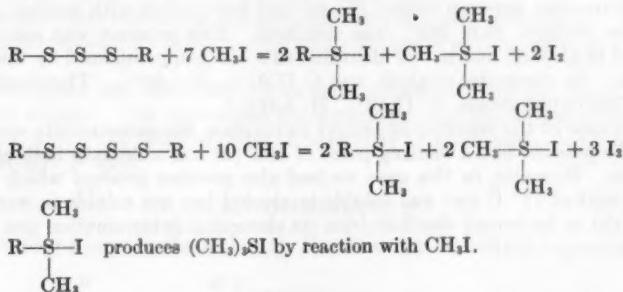
RSH gives RSSR by oxidation in the presence of HI.



Monosulfides give trimethylsulfonium iodide readily at room temperature.



Tri- and tetrasulfides are believed here to have the same reaction mechanisms as the disulfide. Since we did not observe free sulfur, the center sulfur atom is thought to take part in the reaction as follows:



This reaction with  $\text{CH}_3\text{I}$  cannot be considered as resulting from the inductive effect of the  $\text{CH}_3$  group. Therefore, the formation of  $(\text{CH}_3)_3\text{SI}$  is a result of hyperconjugation, which gives a carbonium ion by an electrometric effect.

Ether ( $\text{R}-\text{O}-\text{R}$ ) does not react with methyl iodide. Thioether can react with it by reason of the greater ease of coordination of the free electrons of the sulfur.

*Reaction of tolyl mercaptan, tolyl mono-, di-, tri- and tetrasulfide with methyl iodide.*—Ten cc of methyl iodide was added to 1 g of each sulfide and the mixture then heated for two hours in a sealed tube at  $100^\circ$ . After reaction, methyl

iodide was removed under vacuum. The product was crystallized from alcohol and analyzed. Melting points were as follows:

	-SH	-S <sub>1</sub> -	-S <sub>2</sub> -	-S <sub>3</sub> -	-S <sub>4</sub> -
M.p. Before reaction	43	57	46	76-77	75
After reaction	43	57	46	77	75

From these results, it is seen that no reaction occurred. Trimethylsulfonium iodide was not obtained. Moreover, methyl iodide and free sulfur for two hours at 100° C did not react.

Polysulfides<sup>8</sup>, with sulfur adjacent to aromatic radicals, and elementary sulfur<sup>9</sup>, existing as eight membered rings, do not react with methyl iodide. On the other hand, polysulfides of aliphatic organic compound will react with CH<sub>3</sub>I.

### CONCLUSIONS

Mercaptan and polysulfides of the benzyl and *p*-tolyl series were heated with methyl iodide in sealed tubes for two hours at 100° C with the results:

1. Benzyl mercaptan and benzyl mono-, di-, tri- and tetrasulfide gave trimethylsulfonium iodide.
2. Tolyl mercaptan and tolyl mono-, di-, tri- and tetrasulfides did not react with methyl iodide, contrary to previous thinking for the action of mono and disulfides.
3. Free sulfur did not react with methyl iodide.

### ACKNOWLEDGMENT

The author wishes to thank Professor H. Kambara, K. Fujisawa and Y. Nakajima for their helpful suggestions.

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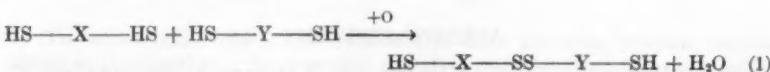
## ORGANIC SULFIDES AND POLYSULFIDES. VI. REACTIONS OF METALLIC OXIDES WITH POLYSULFIDE RUBBERS \*

YUJI MINOURA

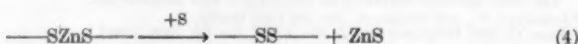
TOKYO TECHNOLOGICAL UNIVERSITY

Polysulfide synthetic rubbers (thiokol Type A, Type FA, LP-2, etc.) can be vulcanized by metallic oxides such as zinc oxide, lead oxide and magnesium oxide<sup>1-3</sup>, or by diisocyanates<sup>4</sup> or by epoxy compounds<sup>5</sup>, and there is no necessity for adding the vulcanizing agents usually used in rubbers. Generally, zinc oxide and lead oxide are used as vulcanizing agents, but the mechanisms of vulcanization are still uncertain.

In this present study polysulfide synthetic rubbers have been prepared by the reaction of dihalogen organic compounds with alkali polysulfides, and most of the end groups of the products are assumed to be mercaptan groups. When blended with metallic oxides and then heated, they combine to make a chain by the following oxidation reaction:



Kirchhof<sup>1</sup> reported that the mechanisms of vulcanization were successive reactions of polymerization as above mentioned. Patrick<sup>2-3</sup> investigated the generation of water in the same reaction. Mercaptans gave rise to mercaptides in the reaction with metallic oxides by heating, and the latter changed to sulfides in the presence of monosulfide and sulfur.

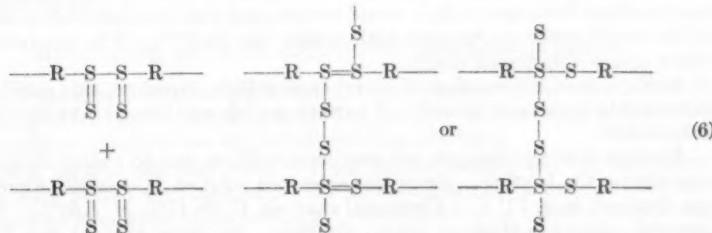
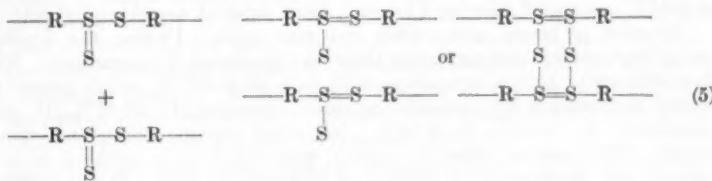


Recently Fettes, Panek and Jorcza<sup>4-5</sup> have concluded that polysulfide rubbers such as Thiokol FA having hydroxy groups at the chain ends, are vulcanized by diisocyanates instead of by metallic oxides, and that vulcanization here too consists of chain extension. Some workers, however, have considered that the mechanism of vulcanization consists of the formation of a molecular network.

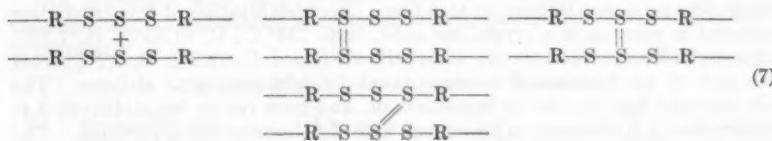
Stocklin<sup>6</sup> has agreed with Patrick who explained that rubbers are changed to an elastic state from a plastic state, but, considering the change in solubilities, he also supposed a network of molecules of polysulfide rubbers to be formed.

\* Translated from *J. Soc. Rubber Ind. Japan* 26, 399-407 (1955).

From an investigation of swelling, Spielberger<sup>7</sup> said that networks are formed in vulcanization as follows:



As the author<sup>8-10</sup> has reported, the sulfur in organic polysulfide compounds is bonded in chain structures. Therefore, even if a network formation takes place, it may be supposed that the reaction will be as follows:



This mechanism of reaction, however, is only provisional and not confirmed. The author has studied and here reports on organic sulfides of low molecular weight in contact with metallic oxides (zinc oxide, lead oxide) at 135° C., and has thus studied the vulcanization mechanism of polysulfide rubbers. From the reaction between benzyl or tolyl sulfides and zinc oxide or lead oxide, many products were isolated but any reaction such as (5), (6), or (7) could not be found. In the polymerization of polysulfide synthetic rubbers, the author has found that the higher the molar ratio of alkali polysulfide to dihalogen compound the lower the amount of halogen as the end group of the high polymer, and the larger the amount of mercaptan end group. That is, most of the end groups of polysulfide synthetic rubber prepared by using a large quantity of alkali sulfide consists of —SH groups. Moreover, the formation of mercaptide, monosulfide or disulfide was established by the reaction of metallic oxides with benzyl or tolyl mercaptans. From these results it was confirmed that reactions occur in accordance with Equations (1) to (4), and that vulcanization is not the result of network formation by a condensation reaction between molecules.

*Sulfides and reagents.*—The low molecular weight organic sulfides were prepared as described in a previous report<sup>11</sup>. The reagents, zinc oxide and lead oxide, were commercial chemicals.

## REACTIONS OF ZINC OXIDE AND ORGANIC SULFIDE

About 1 g of each material was mixed with 2-3 g of zinc oxide and heated at 135° C in a sealed tube for 6 hours. Each product was extracted with ether.

*Reaction of benzyl monosulfide and zinc oxide.*—During the heating of benzyl monosulfide and zinc oxide there was no change in appearance. Extraction with ether gave a crystalline solid, m.p. 48.5-49° C, which proved to be benzyl monosulfide by elemental analysis; observed: C, 78.41%, H, 6.32%; calculated: C, 78.5%, H, 6.54%. No other organic compound was produced. The residue after extraction was added to a solution of sodium arsenite and made acidic by adding of hydrochloric acid. If zinc sulfide had been produced hydrogen sulfide would evolve, and then precipitation of arsenic sulfide would result by reaction with arsenic ion ( $\text{As}^{+++}$ ). The precipitate is yellow and is determined easily.

In the case of the reaction of benzyl monosulfide, therefore, zinc sulfide was shown not to have been formed. No arsenic sulfide was formed from the benzyl monosulfide.

*Reaction of benzyl disulfide and zinc oxide.*—There was no change in appearance during the heating. From the extracted solution, a crystalline product was obtained, m.p. 71° C. Elemental analysis, C, 68.15%, H, 5.52%. These observed values are those of benzyl disulfide. No other product was found. No zinc sulfide was formed. From these results, therefore, benzyl disulfide did not react with zinc oxide.

*Reaction of benzyl trisulfide and zinc oxide.*—While heating, the product became somewhat orange and had a smell of hydrogen sulfide. After extraction with ether and evaporation, an oily material was obtained, in which a white crystalline solid was formed on standing. Recrystallization of this crystalline material in ether gave a crystalline solid, m.p. 124° C; C, 91.85%, H, 7.1%. This crystalline product proved to be stilbene (calcd. C, 92.3%, H, 7.7%) from the fact of no decrease of melting point by admixing with stilbene. The oily material had an odor of benzaldehyde, and gave rise to benzaldehyde 2,4-dinitrophenyl hydrazone on treatment with 2,4-dinitrophenylhydrazine. The hydrazone obtained was crystalline of m.p. 237° C, N content = 19.7% (calculated, 19.5%). A yellow precipitate of arsenic sulfide by reaction of the residue with sodium arsenite and hydrochloric acid showed the presence of zinc sulfide. Hydrogen sulfide, stilbene, benzaldehyde and zinc sulfide therefore are formed from the reaction of zinc oxide and benzyl trisulfide. Benzyl trisulfide gave zinc sulfide by reaction of the sulfur with zinc oxide, and partly gave stilbene. In this reaction we could not find the sulfide compounds, which are shown in Equations (5) and (7).

*Reaction of benzyl tetrasulfide and zinc oxide.*—As in the case of trisulfide, from the reaction of benzyl tetrasulfide and zinc oxide, an orange product was obtained. The oily material, obtained by extraction, formed a white as well as a yellow crystalline solid after a long standing. These crystalline products were recrystallized from alcohol. The yellow solid, m.p. 119° C, was found to be sulfur, by mixed melting point, and when it was burned it formed sulfur dioxide. The white solid, m.p. 124° C, proved to be stilbene (C 92.1%, H 7.5%). In this case also, the oil material had an odor of benzaldehyde. The hydrazone, which was prepared from 2,4-dinitrophenylhydrazine, was identified by elemental analysis. In the analysis of the residue of zinc sulfide, a large quantity of arsenic sulfide was precipitated. Free sulfur, hydrogen sulfide, stilbene, benzaldehyde and zinc sulfide thus were formed in the reaction between zinc

oxide and benzyl tetrasulfide. Neither a dimer nor a trimer which might be supposed to be held together through sulfur as in a tetrasulfide was found.

*Reactions of p-tolyl sulfides and zinc oxide.*—*p,p'*-Tolyl mono-, di-, tri- and tetrasulfide were heated at 135° C in sealed tubes. The formation of zinc sulfide was not found in any such treatment. Unreacted sulfides crystallized out. Recrystallizations gave mono-, di-, tri- and tetrasulfide, which were identified by elemental analysis. In the case of reaction of tri- and tetrasulfide, a small quantity of sulfur was isolated. Though a small quantity of disulfide was probably formed, we could not get a crystalline product.

Tolyl sulfides are more stable than the benzyl sulfides. They do not react with zinc oxide.

#### REACTIONS OF LEAD OXIDE AND ORGANIC SULFIDE

As in the experiments with zinc oxide, 1 g of organic sulfide was mixed with about 3 g of lead oxide, and then heated at 135° for six hours in a sealed tube. Each product obtained was extracted and then identified.

*Benzyl sulfides and lead oxide.*—When benzyl mono-, di-, tri- and tetrasulfide were heated with lead oxide, the monosulfide gave a gray product and the other sulfides gave black products. Identification of metallic sulfide was carried out by adding hydrochloric acid and a solution of sodium arsenite to the residue after extraction. In the reaction of monosulfide a small amount of lead sulfide was formed, but in the case of di-, tri-, and tetrasulfide, much lead sulfide formed. The formation of lead sulfide from disulfide was in less quantity than from tri- or tetrasulfide.

By extraction with ether, white crystals were obtained. The results of melting points and elemental analysis, after recrystallization from alcohol, were as follows:

#### MELTING POINTS AND ANALYSIS OF PRODUCTS

Benzyl sulfide used	M.p.	C, %	H, %
Mono	49	78.51	6.03
Di	71	68.41	5.58
Tri	70.5-71	68.33	5.51
Tetra	71	68.39	5.47

These results show that the products obtained from mono- or disulfide were unchanged starting material. Since lead sulfide, however, was found in the residue in the case of disulfide, it seemed to have reacted but we could not determine the products. The crystalline product obtained from tri- or tetrasulfide was benzyl disulfide, identified by mixed melting point. It was found that tri- and tetrasulfides are easily desulfurized by lead oxide.

Lead oxide is more reactive than zinc oxide. Tri- and tetrasulfides gave disulfide by desulfurization. We believe that the reactions (5), (6) and (7) do not occur with lead oxide and benzyl polysulfide.

*p-Tolyl sulfides and lead oxide.*—As in the case of the benzyl series, *p*-tolyl sulfides were treated with lead oxide under the same conditions. Lead sulfide was determined and the products from extraction were examined. In the case of mono- and disulfide, orange products were observed. Tri- and tetrasulfide gave black products containing large quantities of lead sulfide. After extraction by ether, white crystals were obtained. The results of melting points and

elemental analysis, after recrystallization from alcohol, were as follows:

#### MELTING POINTS AND ELEMENTAL ANALYSIS OF PRODUCTS

<i>p</i> -Tolyl sulfide used	M.p.	C, %	H, %
Mono	57	78.36	6.59
Di	46	68.34	5.74
Tri	46	68.37	5.70
Tetra	46	68.41	5.78

From these results, it was found that mono- and disulfide do not react with lead oxide. The crystals obtained from the tri- and tetrasulfides proved to be *p*-tolyl disulfide. The tri- and tetrasulfides thus were desulfurized by reaction with lead oxide though they were not by zinc oxide. As the products, however, which are shown in Reactions (5), (6) and (7) were not isolated, we suppose these reactions do not occur. In the desulfurization by lead oxide, it was found that the tri- and tetrasulfide in the benzyl series are more reactive than those in the tolyl series.

#### REACTION OF MERCAPTANS WITH ZINC OXIDE OR LEAD OXIDE

As for benzyl and *p*-tolyl sulfides, benzyl mercaptan and *p*-tolyl mercaptan were treated with metallic oxide (lead oxide, zinc oxide) at 135° for 6 hours in sealed tubes.

*Reaction of benzyl mercaptan with zinc oxide or lead oxide.*—Zinc oxide or lead oxide (2–3 g) were put in a glass tube and then benzyl mercaptan (about 1 g) was added. The mercaptan reacted with lead oxide immediately and gave a greenish brown mercaptide. After further reaction by heating, the products were extracted by ether and divided into two parts—the soluble fraction and the residue. Unreacted metallic oxide and its mercaptide were present in the residue. Solutions of sodium arsenite and hydrochloric acid were added to the residue. In the case of both zinc oxide and lead oxide, no precipitate was found showing no formation of metallic sulfides. The presence, however, of arsenic mercaptide and benzyl mercaptan were noted from the turbidity of the solution. These were determined by the characteristic odor of mercaptan and by the formation of benzyl mercaptan on adding lead acetate.

Recrystallization from alcohol of the solid obtained from the ether extract, after removing a small quantity of arsenic mercaptide, gave a white crystalline solid, m.p. 70° C. This solid proved to be identical with benzyl disulfide by elemental analysis as follows

In the case of:	M.p.	C, %	H, %
Zinc oxide	70	68.42	5.75
Lead oxide	70	68.33	5.71

The disulfides were formed by air oxidation during the reaction. Under these conditions, benzyl mercaptan gave mercaptide by reaction with metallic oxide and disulfide by the oxidation with air. From the results neither metallic sulfide nor monosulfide was formed so Reactions (3) and (4) did not occur.

*Reaction of *p*-tolyl mercaptan with zinc oxide or lead oxide.*—As in the case of benzyl mercaptan, *p*-tolyl mercaptan was treated with zinc oxide and with lead oxide. Lead oxide did not produce as exothermic a reaction as it did in the

case of benzyl mercaptan. Mercaptide, however, was produced easily. Reaction with zinc oxide gave a white product, and lead oxide gave a yellow one. The products were extracted with ether and analyzed.

The residues after extraction were treated with hydrochloric acid and sodium arsenite, but gave no precipitate of arsenic sulfide. Therefore no metallic sulfide was produced. The turbidity of solution, however, showed the presence of arsenic mercaptide and tolyl mercaptan.

The ether solution gave crystalline product. Recrystallization from alcohol, in both cases, gave *p*-tolyl disulfide, m.p. 46° C. The results were:

In the case of:	M.p.	C, %	H, %
Zinc oxide	46	68.31	5.67
Lead oxide	46	68.35	5.71

The disulfides were formed by air oxidation. Mercaptides were not removed from the ether solution in these cases.

From these results, it is seen that *p*-tolyl mercaptan reacts with metallic oxide, to give mercaptide easily, and is readily oxidized to disulfide.

The reactions with sulfides and with mercaptans lead to the following conclusions:

Mercaptans react with metallic oxides easily. Sulfides are desulfurized by metallic oxides without establishment of sulfur crosslinks. Qualitatively the benzyl series is more reactive than the tolyl series, and lead oxide more reactive than zinc oxide. Therefore, vulcanization of polysulfide rubber is believed to be a chain growth of molecules.

These conclusions support the fact that the polysulfide synthetic rubbers, which have —SH groups at the ends of molecules, are vulcanized by metallic oxides, diisocyanates or epoxy compounds, and will be vulcanized by compounds having two or more functional groups which react with —SH such as organic peroxides.

TABLE I  
REACTION PRODUCTS OF SULFIDE WITH ZINC OXIDE OR LEAD OXIDE

Sulfide	Reagent	ZnO	PbO
Benzyl mercaptan		Mercaptide (white) Benzyl disulfide	Mercaptide (greenish brown) Benzyl disulfide
Benzyl monosulfide		No reaction	No reaction
Benzyl disulfide		No reaction	No reaction
Benzyl trisulfide		Zinc sulfide Hydrogen sulfide Stilbene Benzaldehyde	Lead sulfide Benzyl disulfide
Benzyl tetrasulfide		Zinc sulfide Hydrogen sulfide Stilbene Benzaldehyde Sulfur	Lead sulfide Benzyl disulfide
<i>p</i> -Tolyl mercaptan		Mercaptide (white) <i>p</i> -Tolyl disulfide	Mercaptide (greenish brown) <i>p</i> -Tolyl disulfide
<i>p</i> -Tolyl monosulfide		No reaction	No reaction
<i>p</i> '-Tolyl disulfide		No reaction	No reaction
<i>p</i> '-Tolyl trisulfide		No reaction	Lead sulfide <i>p</i> '-Tolyl disulfide
<i>p</i> '-Tolyl tetrasulfide		No reaction	Lead sulfide <i>p</i> '-Tolyl disulfide

## SUMMARY

1. Both mercaptides and disulfides were obtained by the reactions between benzyl mercaptan or tolyl mercaptan with zinc oxide or lead oxide. Qualitatively, mercaptides were formed from benzyl mercaptan easier than from tolyl mercaptan, and lead oxide reacted with mercaptan easier than zinc oxide with mercaptan. From the fact that no metallic sulfide was present, disulfides were likely formed from the oxidation of mercaptans by air.

2. The mono- or disulfides of the benzyl and tolyl series did not react with zinc oxide or lead oxide.

3. Neither tolyl tri- nor tetrasulfide reacted with zinc oxide, but benzyl tri- and tetrasulfide reacted with zinc oxide to give zinc sulfide. In the case of benzyl trisulfide, hydrogen sulfide, stilbene and benzaldehyde were formed, and in the case of tetrasulfide, we found the formation of hydrogen sulfide, stilbene, benzaldehyde and sulfur.

4. The tri- and tetrasulfide of both the benzyl and tolyl series reacted with lead oxide and they gave lead sulfide and organic disulfide. That is, they were desulfurized by lead oxide. In these reactions the benzyl series was more reactive than the tolyl series and the tetrasulfide was more reactive than tri-sulfide in the same series.

5. Lead oxide reacted with polysulfide easier than zinc oxide.

6. From the results of reactions between metallic oxide with mercaptan or other sulfide, it was concluded that the vulcanization mechanism of polysulfide rubber by metallic oxide is the reaction represented by Equations (1) to (4), the products being converted to high polymer without formation of a network of polysulfides.

## ACKNOWLEDGMENT

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# CHANGES IN THE ELECTRICAL PROPERTIES OF NATURAL RUBBER/CARBON BLACK COMPOUNDS DURING VULCANIZATION \*

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## FOREWORD

The study of the electrical properties of rubber compounds containing carbon black has various applications. Alternating current properties are important in connection with the quality of wire and cable insulation and the practical development of radio-vulcanization. Direct current properties are essential for designing conductive or antistatic compounds. Moreover, both methods can provide useful data on the distribution of carbon black particles in the compounds, without any risk of disturbing the colloidal structure.

However, direct current conductivity depends upon the fraction of the black in nearly continuous chains of particles, which can conduct the current from one electrode to the other when a sufficient black loading is reached<sup>1</sup>. The remaining black is either isolated particles or agglomerates distributed at random through the rubber; it seems that this second fraction rather influences the AC properties, as shown already by Kickstein<sup>2</sup> and by two of the authors<sup>3</sup>.

We have studied again the factors which affect the electrical properties of black compounds, by operating inside the mold in which the rubber is vulcanized. So may be avoided the heat conditioning required when electrical measurements are made by the conventional method, i.e., with samples tested after removal from the mold. Moreover, it is possible to measure the electrical properties at all stages of vulcanization, especially at the beginning, when the compound is not yet set up.

In the scope of this work, we could investigate only high frequencies and we had to limit our tests to one carbon black type, i.e., Witco MPC Black, modified or not by heat treatment.

Finally, the alternating current properties of compounds have been much more intensively studied than direct current resistivity, the latter being nevertheless necessary to calculate the corrections needed for an accurate evaluation of dielectric properties.

## DESCRIPTION OF THE CONDENSER-MOLD

The vulcanization mold which serves also as test condenser is shown in Figure 1. It includes two steel blocks with sufficient heat capacity to make heat insulation unnecessary. However, the mold can be brought up to a temperature of 100–150° C in a shorter time than required by the compound to reach a uniformly stabilized temperature, i.e., about 3 minutes.

Two cylindrical chambers are bored in the mold, each measuring 25.8 mm diameter by 90 mm long, the axes of which are in the same plan as the joint of

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the mold. A cylindrical steel core, forming a coaxial electrode, 95 mm long, with a variable diameter, is inserted in each chamber. These cores are insulated at both ends by Teflon bearings, while the rest of the mold is grounded. Teflon was chosen as insulator because of its low dielectric constant and good mechanical properties at vulcanization temperatures; moreover, it may be easily machined, so that the cores can be accurately centered.

The rubber testpieces which form the dielectric of the test condenser are consequently hollow cylinders, 70 mm long by 25.8 mm external diameter. This elongated shape helps to minimize disturbances in the electric field close to the ends. The shape of the insulators and the diameter of the cores were also chosen so that the parallel capacity resulting from the insulator—6.2 picofarads or  $\mu\text{uf}$  was small as compared with the capacity of the condenser proper, filled with compound.

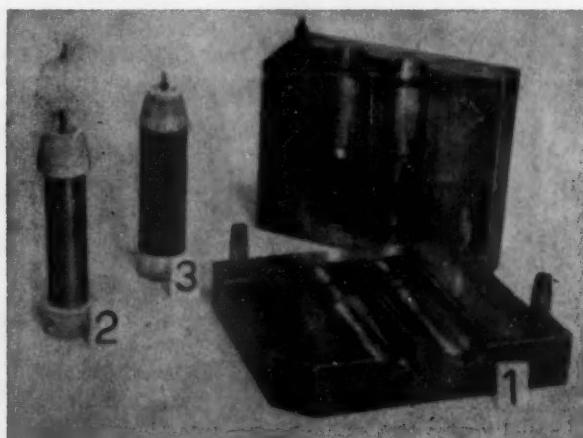


FIG. 1.—Condenser-mold for measuring electrical properties during vulcanization. 1. External electrode. 2. Coaxial internal electrode. 3. Rubber sample covering the internal electrode.

The empty capacity of the capacitor is 15.4 pf with the 20 mm diameter core generally used for these tests. Finally, a small press, with two electrically heated platens, is used to vulcanize the compounds in the condenser at the desired temperature.

#### ELECTRICAL MEASUREMENTS

**Resistivity.**—The resistivity of the testpieces is measured by applying a constant voltage of about 150 v between the inner cylindrical electrode and the mold. The equipment includes an electronic voltmeter and a sensitive galvanometer allowing the determination of resistivities from  $10^6$  to  $10^{13}$  ohm-cm. The contact resistance between the compound and the wall of the mold is found negligible and is not taken into account.

**Dielectric properties.**—The dielectric constant and alternating current losses are measured with a General Radio Schering Bridge between 100 cps and 100 kcps. The voltage at the terminals of the condenser-mold is about 12 volts. The characteristics of the condenser-mold are determined by a substitution

method. As for resistivity, it is verified that the wall contact impedance is negligible.

On the other hand, the indications of the bridge should be corrected by taking into account the stray capacity in the region of the Teflon insulators. The direct current conductivity is also in parallel with the testpiece. Experiments have shown that this conductivity correction is small for frequencies above 1 keps, as long as the carbon black loading is lower than 20% by volume.

The corrected experimental data give the dielectric constant  $\epsilon'$  and the loss factor  $\operatorname{tg} \delta$  of the compound. The latter may consequently be considered as an imperfect dielectric, characterized by a complex dielectric constant:

$$\epsilon = \epsilon' - i\epsilon''$$

the loss being related to the real and imaginary components by:

$$\operatorname{tg} \delta = \epsilon''/\epsilon'$$

#### COMPOUNDING INGREDIENTS AND PROCESSING CONDITIONS

The base compound (Table I) consistently adopted for the majority of these tests has optimum mechanical properties after about 15 minutes of vulcanization at 135° C.

Carbon black is added at 4, 8, 10, 12, 15, 20 and 30 volume per cent of rubber, assuming that the density of the black in the compounds is equal to 1.8

TABLE I  
BASE COMPOUND FOR VULCANIZATION EXPERIMENTS

Crepe	100
Stearic acid	1
Zinc oxide	5
Tetramethylthiuram disulfide (TMTD)	0.3
Sulfur	2.5
Phenyl-2-naphthylamine	1
MPC carbon black	x

g/cm<sup>3</sup>. All the compounds are prepared from the same homogenized crepe batch. It is necessary to determine the mixing conditions very accurately, since they strongly affect the electrical properties of the compounds. The following operating method was chosen somewhat arbitrarily:

400 g crepe is masticated for 3 minutes in an internal Werner laboratory mixer heated at 90° C; the black is then introduced and mixed for 3 minutes; in order to introduce the ingredients, the resulting masterbatch is treated on an open mill (3 mm between rolls, friction 4/3), then passed between the tight rolls and calendered. The whole mixing process takes about 8 minutes.

#### REPRODUCIBILITY OF ELECTRICAL PROPERTIES

The main cause of erratic variations in the electrical properties of the compounds is linked to the configuration of the black particle agglomerates. Such agglomerates are, in particular, oriented by the shearing effects of mixing and molding. Such 'structural' effects, however, are noticeable above a certain level only, i.e., when the black loading exceeds some 8% by volume. To control

these effects, the mixing schedule must be followed accurately, and care should be taken:

- (a) to calender to about the thickness of the molded testpiece.
- (b) to always cut the blank along the same direction of calendering, and at a constant volume not much larger than the testpiece volume.
- (c) to always apply about the same pressure on the mold when closing the press.

Despite better reproducibility realized by this procedure, the scattering of the results is still much higher than the errors of the measurements and increases with the black loading (Table II).

TABLE II  
VARIATIONS  $\Delta\epsilon$  AND  $\Delta tg \delta$  OF THE DIELECTRIC CONSTANT AND LOSS FACTOR OF COMPOUNDS IN THE CONDENSER-MOLD

Black loading, vol. %	Samples from same mix		Samples from different mixes	
	$\Delta\epsilon$ :%	$\Delta tg \delta$ %	$\Delta\epsilon$ :%	$\Delta tg \delta$ %
8	$\pm 1$	$\pm 2$	$\pm 2$	$\pm 4$
20	$\pm 4$	$\pm 5$	$\pm 6$	$\pm 8$

#### ORIENTATION EFFECTS OF MIXES IN THE MOLD

Up to an MPC black loading of 10% by volume, the dielectric properties of the mixes are not altered when the 20 mm diameter core is used instead of the 15.8 mm diameter core. Conversely, when this loading is exceeded,  $\epsilon'$  and  $tg \delta$  are increased when the dielectric is thinner, and the more so when the loading is higher (Table III).

This peculiarity may be tentatively interpreted in three ways, i.e., by the contact impedance between the compound surface and the mold wall, by variation of the electric field applied to the testpiece, or by an eventual variation in the dielectric properties of the compound.

With the first assumption, volume and surface impedances may be calculated on the basis of the surface-volume ratio of the testpiece, and consequently of its thickness. By using the above-mentioned experimental data in the theoretical relations obtained in this way, we get negative values for contact resistances and capacities. Since this is clearly an absurd conclusion, the thickness effect cannot be explained by the contact impedance.

In the same way, variations of the electric field cannot be the cause, since the dielectric properties of the compounds do not change when the voltage on the condenser varies from 1 to 12 volts for the same core.

The last and most probable assumption was that the nature of the material varies with the size of the core and the degree of orientation inside the mold. In order to check the influence of this last factor directly, we duplicated the method used by Scott<sup>4</sup> to change in a large way the orientation of whiting or zinc oxide compounds. It consists in preparing blanks shaped nearly as the molded testpiece, and other blanks with very different shapes. In this way, the compound suffers a minimum or maximum deformation—and orientation—when the mold is closed. During vulcanization in the condenser-mold, differences of dielectric properties were found in the same direction and of the same order as when changing the core diameter. It seems, therefore, that the deter-

TABLE III  
INFLUENCE OF MOLDING THICKNESS ON THE DIELECTRIC PROPERTIES AT 1 KOPS AFTER VULCANIZING  
ONE HOUR AT 135° C.

Thickness (mm)	Carbon black loading (vol. %)					
	4		8		12	
	$\epsilon'$	$tg \delta \times 10^3$	$\epsilon'$	$tg \delta \times 10^3$	$\epsilon'$	$tg \delta \times 10^3$
2.9	3.17	0.98	4.02	1.69	4.48	2.11
5	3.17	0.96	4.02	1.63	4.48	1.98

Thickness (mm)	Carbon black loading (vol. %)					
	10		12		15	
	$\epsilon'$	$tg \delta \times 10^3$	$\epsilon'$	$tg \delta \times 10^3$	$\epsilon'$	$tg \delta \times 10^3$
2.9	3.17	0.98	4.02	1.69	4.48	2.11
5	3.17	0.96	4.02	1.63	4.48	1.98

Thickness (mm)	Carbon black loading (vol. %)					
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	10		12		15	
	$\epsilon'$	$tg \delta \times 10^3$	$\epsilon'$	$tg \delta \times 10^3$	$\epsilon'$	$tg \delta \times 10^3$
2.9	3.17	0.98	4.02	1.69	4.48	2.11
5	3.17	0.96	4.02	1.63	4.48	1.98

20

 $\delta' \times 10^3$ 

32

18

32

18

mining factor is the 'oriented structure' in both cases, so that one may foresee a noticeable dielectric anisotropy of the compounds with sufficient black content.

For the following tests, it was arbitrarily decided to use only the 20 mm diameter core, and consequently a 2.9 mm molding thickness, so as to keep constant the degree of orientation at equal black loadings in the compounds. Strictly speaking, the dielectric properties of the compounds containing more than 10% by volume of MPC black would only be well defined values if this degree of orientation could be specified. Actually, it is difficult to pin down this important factor, except grossly by the thickness of the molded compound.

#### PROCESSES RELATED TO DIELECTRIC PROPERTIES OF COMPOUNDS IN THE MOLD

A systematic study of the different factors which influence the dielectric properties of the compounds in the mold—field frequency, mold temperature, compounding, black loading—leads, as we shall see to a set of apparently complex data. This is why it is difficult to describe as clearly as desirable the effect of each factor, considered individually. Anticipating slightly the conclusions of this study, we shall rather try to show how each such factor is promoting—in varying degrees—one of the processes upon which the dielectric properties of the compounds depend in last analysis, at least in the relevant ranges of frequency and temperature.

TABLE IV  
SPECIAL COMPOUNDS FOR THE PRELIMINARY EXPERIMENT

	Compounds			
	A	B	C	D
Crepe	100	100	100	100
Stearic acid	1	1	1	1
Zinc oxide	5	5	5	5
TMTD	0.3	0.3	—	—
Sulfur	2.5	2.5	2.5	—
MPC black	18	—	18	18

According to recent literature, such processes may originate either from chemical vulcanization reactions, or from change of colloidal structure, in particular of the oriented state of agglomerates of black particles.

The following preliminary experiment was designed to bring out the respective influence of each of these processes on the evolution of dielectric properties. The four compounds indicated in Table IV, were prepared with the help of the forementioned technique, to ensure the reproducibility of the tests.

Compounds A and B are vulcanizable, but only compound A is filled, B being of the gum type. Both C and D compounds are filled but not vulcanizable, although C contains some sulfur.

The dielectric properties were measured in the mold at 135° C and 1 kcps frequency, i.e., the conditions which allow a better differentiation between 'structure' and vulcanization effects respectively. The evolution of properties with heating time is shown in Figures 2 and 3, where it can be noted that:

(1) The dielectric properties of compounds C and D remain identical throughout the experiment, which proves that the presence of sulfur has no influence when vulcanization does not occur.

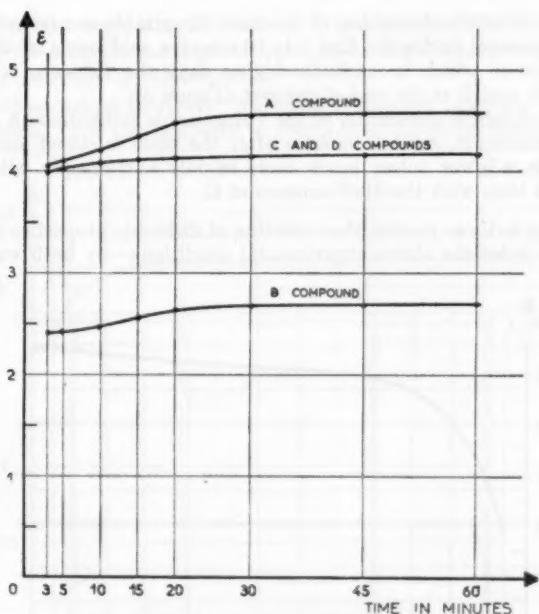


FIG. 2.—Evolution of dielectric constant  $\epsilon'$  during heating at 135° C of compounds A, B, C, D at a frequency of 1 keps.

(2) The dielectric constant of the vulcanizable compounds A and B increases more sharply during the first 20 minutes of heating than the dielectric constant of the nonvulcanizable compounds C and D, and is thereafter fairly constant in all cases (Figure 2).

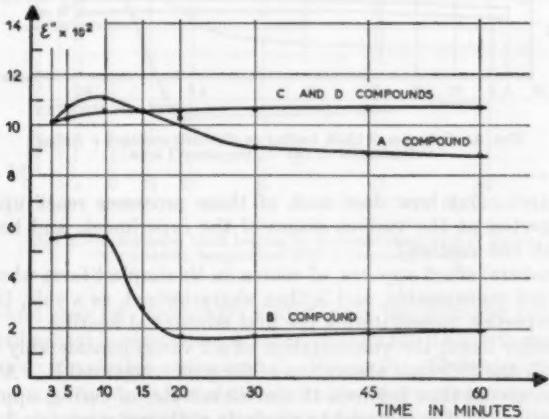


FIG. 3.—Evolution of dielectric absorption  $\epsilon''$  during heating at 135° C of compounds A, B, C, D at a frequency of 1 keps.

(3) The dielectric absorption of the nonvulcanizable compounds C and D is slightly increased during the first 5 to 10 minutes, and levels off thereafter to a constant value which is markedly higher than the values of vulcanizable compounds A and B at the end of the test (Figure 3).

(4) The dielectric absorption of the vulcanizable compounds A and B goes through a maximum, some 8 minutes after the mold is closed, and levels off later towards a lower value, much more rapidly and steeply with the gum compound B than with the filled compound C.

According to these results, the evolution of dielectric properties is obviously influenced—under the above experimental conditions—by both vulcanization

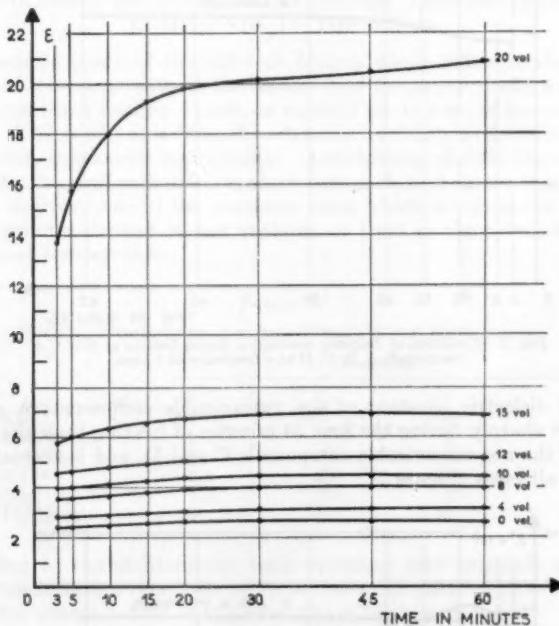


FIG. 4.—Influence of black loading on dielectric constant  $\epsilon'$  during vulcanization at  $135^\circ\text{C}$ , frequency 1 keps.

and 'structure'. But how does each of these processes react upon the dielectric properties at the various stages of the experiment, and how do they interfere with one another?

The 'structure' effect appears, of course, in its simplest form when the compounds are not vulcanizable, and is then characterized, as a rule, by constant dielectric properties, except during the first minutes of heating.

On the other hand, the vulcanization effect varies considerably during the test, especially the dielectric absorption of the gum compound B. A rapid drop in absorption occurs then between 10 and 20 minutes of curing, approximately the time required by the material to reach its optimum mechanical properties, at the end of the chemical reactions of vulcanization.

Except at the beginning of heating, it appears that the contribution of 'structure', for a compound with 10 volumes of MPC black, is already much larger than the effect of vulcanization.

This 'vulcanization-structure' interference does not influence the dielectric constant much. For this property, it seems that the respective effects of vul-

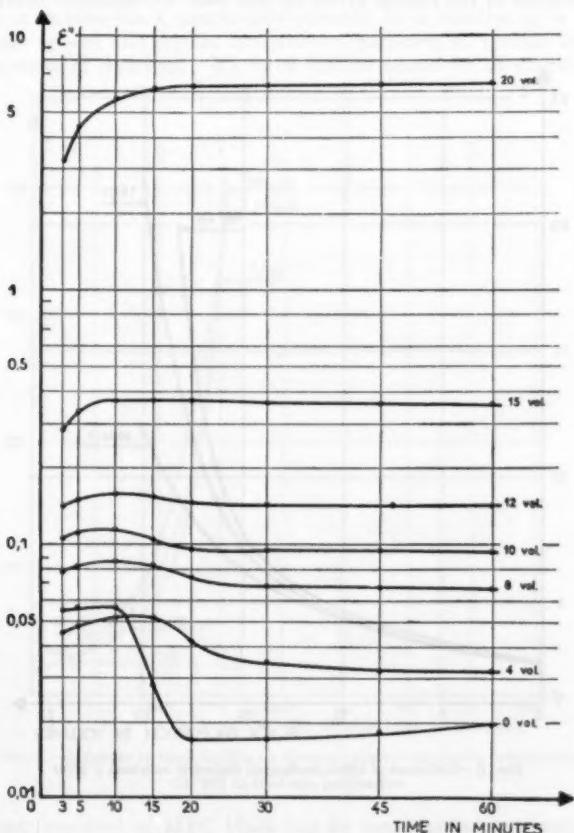


FIG. 5.—Influence of black loading on dielectric absorption  $\epsilon''$  during vulcanization, temperature 135° C frequency 1 keps.

cationization and structure are simply added, since the dielectric constant of the filled and vulcanizable compound A is higher than the dielectric constant of the filled but nonvulcanizable compound C (Figure 2). Conversely, the absorption of compound A, which has about the same value as for compound C at the beginning of vulcanization, falls thereafter to a markedly lower level, without reaching, however, the level of the gum compound B (Figure 3).

In this way, the general contribution of vulcanization to the dielectric absorption of the filled compound A is rather negative, while its contribution to the dielectric constant is constantly positive. But these conclusions should not be endowed with too general value and should be considered rather as tendencies either amplified or reduced by any modifications of frequency, temperature, or MPC black loading. We shall now study these three factors individually, on the basis of the results given by the base vulcanizable compounds of Table I.

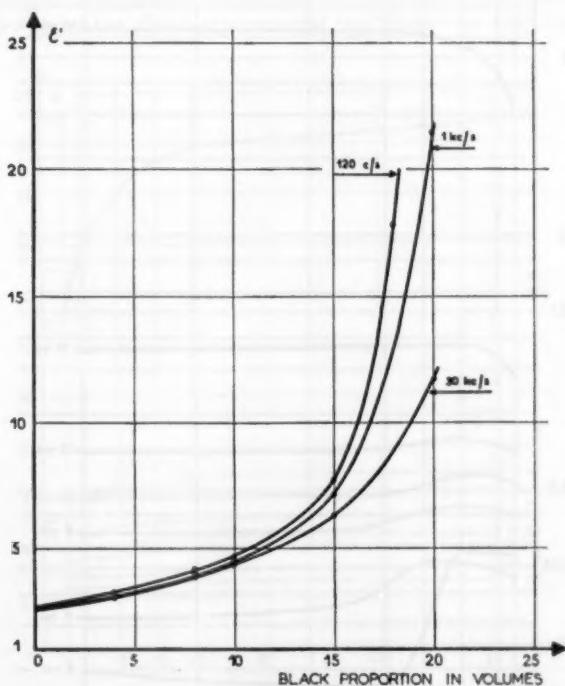


FIG. 6.—Influence of black loading on dielectric constant  $\epsilon'$  after vulcanizing one hour at  $135^\circ\text{C}$ .

#### RELATIONS BETWEEN THE 'STRUCTURE' OF CARBON BLACK AND THE ELECTRICAL PROPERTIES

At a frequency of 1 kcps, the effect of 'structure' is mainly revealed by a general uplifting of the curves of dielectric properties against heating time, when the MPC black loading in the compounds is increased (Figures 4 and 5).

This uplift is not proportional to the black loading. It remains relatively low up to about 10% by volume. Afterwards, the properties increase much more rapidly as indicated by Figures 6 and 7, which give the values found after vulcanizing for one hour at  $135^\circ\text{C}$  and various frequencies.

In this respect, it is clear that a certain parallelism exists between the dielectric losses at low frequency and the direct current conductivity of rubber-MPC black compounds, since the conductivity is also rising rapidly with the black loading above 15% by volume (Figure 8).

However, 'structure' depends not only on the ratio of black, but on mixing and vulcanizing conditions, as well as on the nature of the black. It is not surprising, therefore, that the agglomeration of particles—and thus the electrical properties of rubber-black compounds—should be a function of a variety of factors, such as size and crystal structure of particles, or specific surface and volatile content of powders. We have limited ourselves to examining what

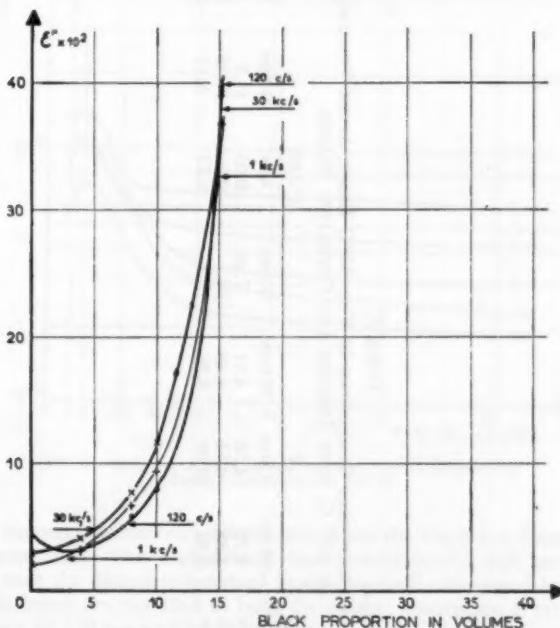


FIG. 7.—Influence of black loading on dielectric absorption  $\epsilon''$  after vulcanizing one hour at  $135^\circ\text{C}$ .

effect a heat treatment of MPC black has on compounds containing 10% by volume of filler and vulcanized at  $135^\circ\text{C}$  in the condenser mold. Samples of this black were placed in a closed porcelain crucible and submitted for two hours to temperatures of  $500^\circ\text{C}$  and  $1,000^\circ\text{C}$  in an electric oven. According to previous work<sup>5,6</sup>, such treatments do not change the size of particles, but reduce the volatile content considerably and graphitize the black.

Variations in the dielectric properties of compounds with heating time do not differ strikingly from what happens with untreated blacks under the same conditions. However, significant differences appear between the levels of such properties as noted in Table V, which gives the values after 60 minutes of vulcanization with untreated and treated black, respectively.

TABLE V  
DIELECTRIC PROPERTIES OF COMPOUNDS CONTAINING 10 VOL. MPC BLACK AFTER VULCANIZING ONE HOUR  
AT 135° C. WITH TREATED AND UNTREATED BLACKS

Conductivity ohm <sup>-1</sup> cm <sup>-1</sup>	$\epsilon'$			$\epsilon'' \times 10^6$			$\log \frac{A}{\epsilon} \times 10^6$		
	120 cps	30 kcps	1 kcps	120 cps	1 kcps	30 kcps	120 cps	1 kcps	30 kcps
Untreated black	3.0 <sup>-13</sup>	4.70	4.56	4.31	7.99	10.05	11.7	1.70	2.71
Black treated at 500°C	3.10 <sup>-13</sup>	4.88	4.71	4.48	11.1	10.9	11.45	2.27	2.32
Black treated at 1,000°C	4.610 <sup>-12</sup>	5.63	5.50	5.28	12.4	9.73	8.91	2.20	1.50

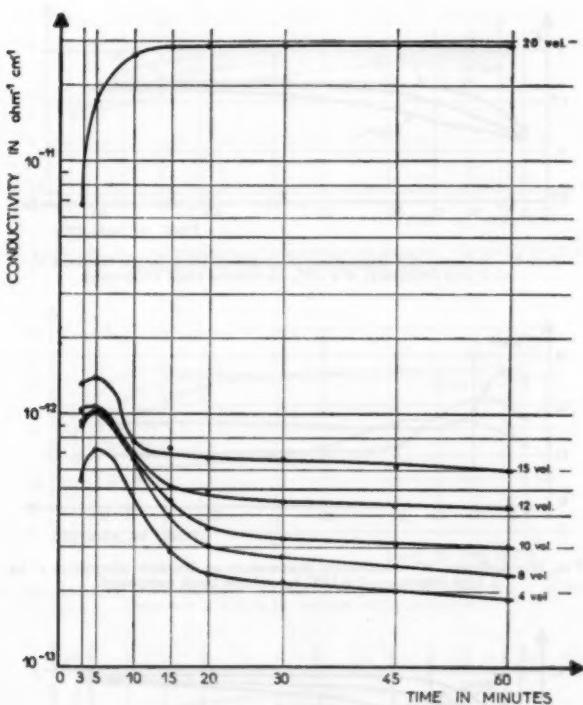


FIG. 8.—Influence of black loading on direct current conductivity during vulcanization at 135° C.

Direct current conductivity is increased when the black has been treated at high temperatures. This had already been established<sup>5,6</sup>, but here we note, moreover, that the dielectric constant is also markedly increased by the treatment, while losses are modified in both directions: absorption is stronger with treated black at 120 cps and lower at 30 kcps.

#### RELATIONS BETWEEN 'VULCANIZATION' AND ELECTRICAL PROPERTIES

The influence of the rate of vulcanization reactions appears in Figures 9 and 10, which show the effect of mold temperature on the dielectric properties, at 1 kcps, of a compound with 10% by volume of MPC black. For both absorption and dielectric constant, a temperature rise from 125° C to 150° C reduces the heating time required to reach the maximum values of these properties during the initial period of curing. The same holds for 120 cps and 30 kcps frequencies, as shown in Figures 11, 12, 13 and 14.

If we study now the further evolution of the properties, we find:

- (a) the dielectric constant bends asymptotically to a limit (Figures 9, 11, 13).

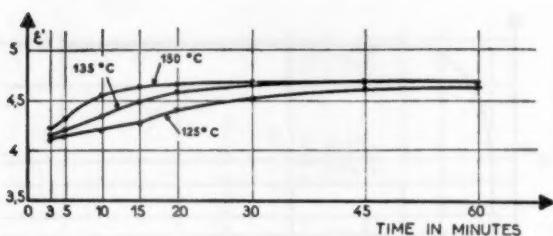


FIG. 9.—Influence of vulcanization temperature on dielectric constant  $\epsilon'$ , at 1 keps frequency, of a 10% by volume black compound.

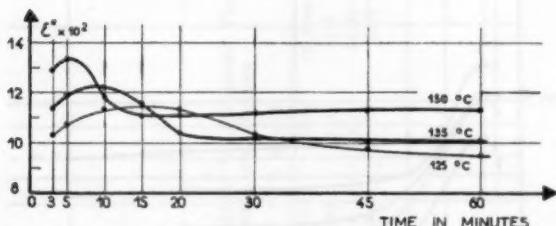


FIG. 10.—Influence of vulcanisation temperature on dielectric absorption  $\epsilon''$  at 1 keps frequency of a 10% by volume black compound.

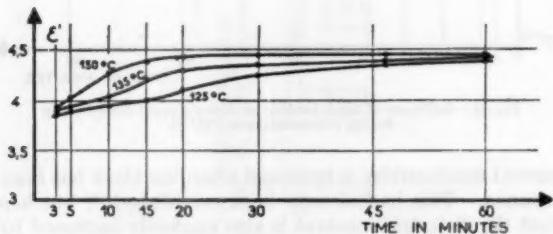


FIG. 11.—Influence of vulcanization temperature on dielectric constant  $\epsilon'$  at 120 cps frequency of a 10% by volume black compound.

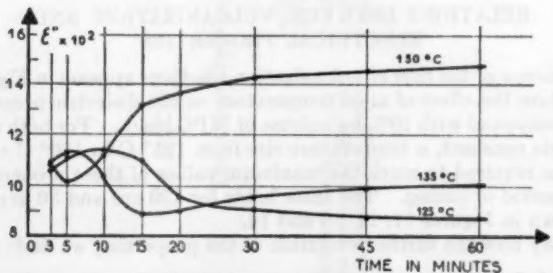


FIG. 12.—Influence of vulcanization temperature on dielectric absorption  $\epsilon''$  at 120 cps frequency of a 10% by volume black compound.

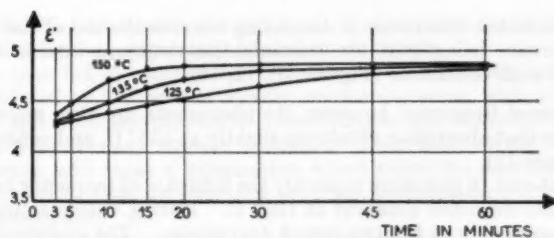


FIG. 13.—Influence of vulcanization temperature on dielectric constant  $\epsilon'$  at 30 kc/s frequency of a 10% by volume black compound.

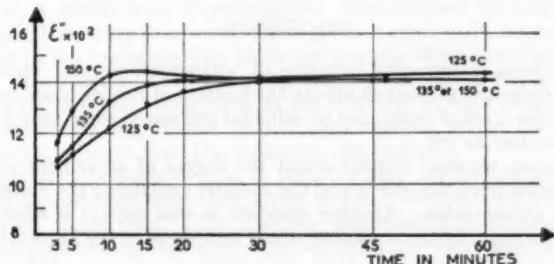


FIG. 14.—Influence of vulcanization temperature on dielectric absorption  $\epsilon''$  at 30 kc/s frequency of a 10% by volume black compound.

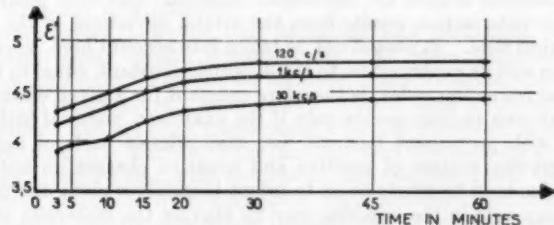


FIG. 15.—Influence of frequency on dielectric constant  $\epsilon'$  of a 10% by volume black compound during vulcanisation at 135°C.

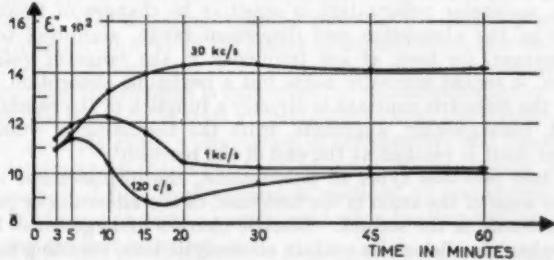


FIG. 16.—Influence of frequency on dielectric absorption  $\epsilon''$  of a 10% by volume black compound during vulcanisation at 135°C.

(b) the dielectric absorption is decreasing towards the end of the vulcanization, the surmise being that the vulcanization-structure interaction is still acting under such conditions (Figures 10, 12, 14).

At the lowest frequency, however, the phenomena are even more complex, since we note that absorption climbs up slightly at 135° C, and considerably at 150° C (Figure 12).

Figures 15 and 16 give more explicitly the influence of frequency on both the absorption and dielectric constant at 135° C. During vulcanization, absorption is decreased only at the two lowest frequencies. The evolution of the dielectric constant is not affected by the frequency, and we simply note that this constant grows smaller with the frequency, contrary to the absorption.

#### DISCUSSION

We have been interpreting in terms of 'vulcanization' and 'structure' the evolution of dielectric properties during the heating of rubber black compounds. Each one covers a set of molecular or colloidal processes, some aspects of which are not quite clear as yet.

Nevertheless, we may wonder about the degree of agreement existing between the results from this study and the theories explaining the dielectric properties of the vulcanizates. Another question in this respect is what contribution may be brought by the condenser-mold technique to the knowledge of such phenomena.

The behavior of gum vulcanizates in an alternating current field is similar to the behavior of viscous polar liquids and arises from three polarization phenomena of different origins, i.e., electronic, molecular and ionic polarization.

Electronic polarization results from the orbital deviations of the electrons, by the electrical field. It should not be taken into account here, since it causes no absorption and its contribution to the dielectric constant, equal to the square of the optical refraction index, is therefore constant for a given elastomer.

Molecular polarization occurs only if the examined material includes electric dipoles with permanent moment, i.e., molecules or parts of molecules in which the gravity centers of positive and negative charges do not coincide. Such molecules tend to rotate so as to orient themselves along the field, while thermal energy acts in the opposite way by stirring the molecules at random. In the case of natural rubber vulcanizates the dipoles are formed during cure at the points of the macromolecular chains where sulfur atoms are chemically fixed. The remainder of the chains is not polarized. Contrary to electronic polarization, molecular polarization is sensitive to changes of frequency and temperature in the absorption and dispersion range, according to Debye's theory. However, for tests at low frequency in the range of vulcanization temperatures, it should normally cause but a negligible absorption. Its contribution to the dielectric constant is directly a function of the combined sulfur content and, consequently, augments, from the beginning of vulcanization, until a higher limit is reached at the end of the reaction<sup>7</sup>.

For the two previous types of polarization, the displacement of charges occurs on the scale of the atom in the first case, of the molecules or polar group of a macromolecule in the second. Electric charges undergo much larger displacements when the dielectrics contain electrolytic ions, resulting for instance from the dissociation of impurities. Sometimes such ions may cross from one electrode to the other through the dielectric and carry a continuous current, just

as in liquids. In other cases, the conductivity is not noticeable and the displacements of ions are apparently limited in amplitude.

We are thus led to consider the dielectric as an essentially heterogeneous medium, formed by a cluster of weakly conducting areas, with different conductivities and dielectric constants. According to the Maxwell-Wagner theory, the ions accumulate, at each oscillation of the field, at the interfaces of adjacent areas, and cause a polarization which raises the dielectric constant. On the other hand, when the ions cross the areas, the resulting friction is a cause of energy absorption.

Except at higher temperatures, this ionic polarization has, in general, a negligible effect on vulcanizates especially with natural rubber, which contains, in the raw state, but a very low proportion of ionizable impurities.

However, a fourth type of polarization, characterized by large amplitude electronic displacements inside the heterogeneous semiconducting areas, seems to dominate in the rubber-carbon black compounds where the above described 'structure' effects occur. The resistance met by the free electrons is small inside black particles, more important at the interface between neighboring particles and extremely large at the ends of agglomerates, where the interval between particles is larger than the molecular dimensions.

Consequently, the agglomerates of particles play, for the electrons, the part of variously shaped semiconducting areas, in which they can move according to the attraction of the field. The resulting polarization is accompanied by a "Joule" energy at the points where the particles are very close to each other. The Maxwell-Wagner theory of heterogeneous media applies again to this 'structure' polarization, which is betrayed by variations in the dielectric constant and loss factor as a function of the frequency, of the same sort as for ionic and molecular polarizations<sup>8</sup>.

Experience shows, however, that molecular and 'structure' polarizations differ strongly under certain circumstances. At radio frequencies, and in vulcanizates with colloidal blacks, for instance, losses are noted which are nearly independent of temperature. Such losses add up to those resulting from molecular polarization and are closely associated with the 'structure' of the black<sup>9</sup>.

This observation is in line with the fact that such vulcanizates present, in the low frequency range, a maximum absorption, also associated with the 'structure' and not much influenced by temperature, while another maximum absorption due to molecular polarization occurs independently from the former, at radio frequencies when the temperature is not too low<sup>8</sup>.

On the whole, molecular, ionic and electronic 'structure' polarizations can all three intervene in the dielectric properties of the compounds heated in the condenser-mold, this technique offering however a possibility of estimating their relative importance at all the stages of vulcanization or heating.

From Figure 3, it seems that the configuration of the agglomerates responsible for 'structure' polarization is influenced by vulcanization, since after sufficient heating, the losses differ from vulcanizable to nonvulcanizable compounds.

A study covering much wider ranges of temperature and frequencies is required to determine on the basis of the Maxwell-Wagner theory, in what way the configuration of such agglomerates is modified by vulcanization. Apparently, this configuration remains unchanged when heating without vulcanizing, except during the first minutes.

Vulcanization has a much stronger influence on molecular and ionic polarization than on structure polarization. As expected, the molecular polarization

of the Debye type rises progressively during the effective vulcanization period, since we note a progressive and limited increase of the dielectric constant, no doubt caused by a polar fixation of sulfur by the polymer. The losses are not affected by this process, because the conditions where the corresponding absorption might occur are far outside the reach of our tests.

Finally, ionic polarization explains both the minimum loss at 120 cps when the black loading in the vulcanizates is around 5% (Figure 7) and the sudden decrease in losses at 1 kcps, during the vulcanization of a gum compound (Figure 3).

In the first case, the ions resulting from the dissociation of nonrubber elements or vulcanizing ingredients are apparently adsorbed by the colloidal carbon black and the losses decrease when the black loading is raised, until this trend is reversed by 'structure' polarization. In the second case, the lower losses suggest that the dissociation processes stop at a certain stage of the reaction, and that the concentration of ions in the compounds is reduced correspondingly. The adsorption of ions by carbon black could also account for the near disappearance of this mechanism of losses in the highly loaded black compounds.

### CONCLUSIONS

To conclude, let us sum up the advantages of direct current or low frequency measurement of the electrical properties of natural rubber compounds, when operating inside the mold in which vulcanization is occurring.

In this way, it is possible to follow the changes in properties during heating or vulcanization more closely and accurately than when operating with samples outside the mold. An orientation of the colloidal structure of compounds above 10% by volume of MPC black is thus easily demonstrated. The dielectric properties of the compounds depend, in this case, on the size of the samples, since this orientation is a function of the dimensions, especially of the thickness of the molded compound.

On the other hand, from the behavior of vulcanizable and nonvulcanizable compounds, a distinction may be made between the respective effects of both the vulcanization and the special state of agglomeration of the black colloidal particles in the compounds.

This 'structure' of the black affects apparently both the losses and the dielectric constant through an electronic polarization phenomenon which can, in principle, be analyzed through the Maxwell-Wagner general theory of heterogeneous dielectrics.

The effect of 'structure' on low-frequency losses depends essentially upon the nature and ratio of the black and varies like direct current conductivity. This 'structure' seems to be influenced also—although to a much smaller extent—by vulcanization, since the level of losses during heating is lower than with a nonvulcanizable compound containing the same ratio of black.

When this ratio does not exceed 10% by volume, vulcanization governs the dielectric properties more directly, both by a fixation of polar sulfur to molecular chains, and by an ionic dissociation of vulcanizing ingredients.

In the range of this study the only effect of molecular polarization is a rather limited increase of the dielectric constant; the losses are not affected. The sudden decrease of losses noted during the vulcanization of a gum compound is explained by a disappearance of the ions formed by the vulcanization reactions. This ionic polarization of the Maxwell-Wagner type plays no marked part in

compounds containing large amounts of black, no doubt because the ions are adsorbed by the black.

By extending this study, as it is hoped, into the field of radio frequencies, it should be possible to improve the theory of the evolution of dielectric properties during vulcanization. From the practical point of view, such work would provide useful experimental data for a rational application of radio-vulcanization.

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## TIRE ABRASION AT DIFFERENT TEMPERATURES \*

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### INTRODUCTION

In previous work<sup>1</sup>, it was shown how reliable results can be obtained in the study of such an apparently variable process as the abrasion of automobile tires. In order to obtain these results it is clear that it is necessary to find the right combination of research equipment, statistical calculations and reliable scientific methods for measurement. Thus it is clear that the use of the so-called "standard test", introduced by the Rubber-Stichting, is advisable. Such a standard test lasts only a short time, hence it is possible to carry it out under fairly constant conditions. If proper precautions are taken, the short standard test gives a sufficiently reliable and statistically accurate picture of the actual abrasion of automobile tires.

One of the most important specifications for the standard test is that the experimental results must be expressed in relative figures. With every compound that is used in the tests, one gets the so-called "relative-abrasion resistance" with reference to a comparison or standard compound, which is run on another wheel in the same test. This relative abrasion resistance has the great advantage that it is only slightly dependent upon experimental conditions. This dependence is much greater for the "absolute abrasion". Thus, for instance, slight variations in the moisture on street surfaces have a strong influence on absolute abrasion. However, it is very difficult to establish what factors are responsible for the differences in the absolute abrasion. It is apparent that many factors have analogous (multiplicative) effects on different compounds, so that these factors may be largely eliminated in a standard test by calculations of the geometric mean values for relative abrasion resistance.

The results of standard tests soon showed that the relative abrasion resistance of two compounds is not constant under all conditions. Above all, the ambient temperature which is determined largely by climate and season of the year, evidently had a profound effect on the relative abrasion resistance. This showed that the relative abrasion resistance for a tire tread X compared with a standard type A, was strongly dependent on the surrounding temperature, other conditions being the same.

Series of standard tests were set up for ambient temperatures varying from about 0° to about 30° C, using a number of tread compounds which are of current interest for passenger car tires. These tests were made with 6.70-15 size tires which were provided with the following types of treads: Natural rubber/HAF (control compound); SBR cold rubber (Polysar Krylene)/HAF; natural rubber/SAF; natural rubber/ISAF; natural rubber/HAF, oil extended and

\* Translated for RUBBER CHEMISTRY AND TECHNOLOGY by W. D. Wolfe, from *Kautschuk und Gummi*, Vol. 10, No. 8, pages WT204, 206 and 208, August (1957). Report No. 317a (1956) of the Rubber-Stichting, Delft, Holland. The present address of G. J. van Amerongen and J. F. Benders is Koninklijke/Shell Laboratory, Amsterdam, The Netherlands and of H. C. J. de Decker is U. S. Rubber Company, Passaic, New Jersey.

TABLE I

	Natural rubber		Synthetic rubber
	Normal	Oil extended	
Rubber (RSS 1)	100	100	—
Polysar Krylene (SBR)	—	—	100
Zinc oxide	5.0	6.2	5.0
Stearic acid	2.0	2.5	2.0
Sulfur	2.5	2.5	2.0
Phenyl-2-naphthylamine	1.0	1.2	1.0
Dutrex 55	3.0	25.0	5.0
Santocure*	0.6-0.9	1.1	1.6
Vultrol ((C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> NNO)	0.0-0.5	0.0-0.5	—
Carbon black**	50.0	62.5	50.0
Vulcanization conditions:			
Hot water at 150° C, minutes	60	60	70 + 10 to cool in press
Circulating heat at 138° C, minutes	60	60	70 + 10 to cool in press

\* Benzothiazolyl N-cyclohexylsulfenamide.

\*\* Carbon blacks used: Vulcan 3(HAF); Vulcan 6(ISAF) and Vulcan 9(SAF).

natural rubber/ISAF, oil extended. Optimum vulcanization for each compound was determined by laboratory tests. The data for compound compositions and vulcanization are given in Table I.

#### THE PROBLEM OF ABSOLUTE AND RELATIVE ABRASION

The standard test provides the absolute abrasion (for example in g/1000 km) along with the relative abrasion resistance of a compound under the test conditions. This absolute abrasion, as previously mentioned, is quite variable for one and the same compound in different tests. It is clear that the dependence of the relative abrasion resistance upon the ambient temperature must, in the final analysis, be caused by the dependence of the absolute abrasion on this temperature. For practical purposes, it is very important to know this latter dependence. Because of the many possibilities for variation in the absolute abrasion, this dependence on temperature for a given compound can be determined with satisfactory accuracy only when a number of measurements are made of the absolute abrasion at different temperatures. The number of compounds for which the dependences on temperature is to be measured is great, so that extensive series of individual tests must be made.

The adequate degree of accuracy with which the relative abrasion resistance of different compounds may be determined in standard tests, offers the possibility of obtaining an approximately accurate idea of the absolute abrasion of a compound at various ambient temperatures. A great many values for the absolute abrasion of one of the compounds were determined. This was the natural rubber/HAF control compound. These results gave a means of evaluating the effect of surrounding temperature on the absolute abrasion of this compound with satisfactory accuracy. A variety of data are available in the literature for similar compounds, so that our results may be compared therewith.

## THE ABSOLUTE ABRASION OF THE CONTROL TIRES

The desired temperature dependence of the absolute abrasion could be derived for the natural rubber/HAF compound from the results of about 100 standard tests. These tests were all run with a Ford "Mainline" on one and the same course in Holland. The abrasion data are plotted in Figure 1. In this figure, not the absolute abrasion but its logarithm was plotted against ambient air temperature. This was done on the basis of considerations by Stiehler, Richey, Steel and Mandel<sup>2</sup>, who found that the influence of weather conditions on the absolute abrasion of automobile tires is multiplicative rather than additive. This could be verified by our own experience. The correlation coefficient determined for about 100 measurements stands at about 0.64. Hence it can be concluded that there is a positive correlation between absolute abrasion and ambient temperature. The distribution of the points is too scat-

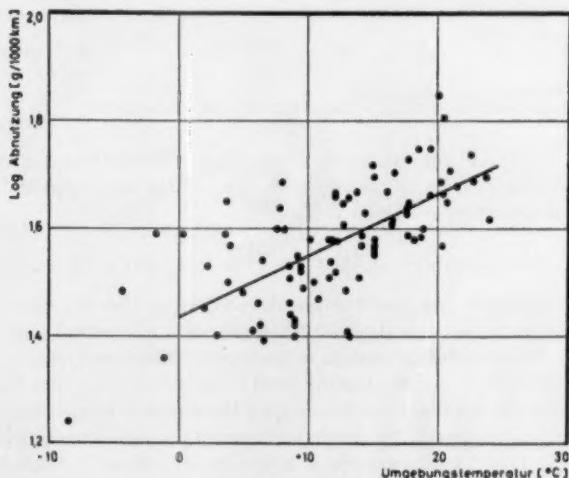


FIG. 1.—Abrasion of natural rubber/50 parts HAF treads in standard test at various temperatures. Abscissa is ambient temperature in °C; ordinate is log abrasion (g/1000 km).

tered to allow us to say that the correlation is anything but linear. The best straight line, to represent the experimental points, was determined with the help of the method of least squares.

Following the train of thought expressed in the second section, this optimal estimate of the relation between absolute abrasion and ambient air temperature taken from Figure 1 was employed as the key to reading off the absolute abrasion of various tire treads. For better clarity, the straight line of Figure 1 was transposed into a curve in linear plots. This curve appears as the comparison curve in Figures 2, 3, and 4. All other curves may now be determined from the abrasion resistance secured by standard tests. Also, for control purposes, the abrasion data of Amon and Dannenberg<sup>3</sup> for similar compounds are plotted in Figure 2. These workers measured the abrasion in terms of loss of depth of the tread grooves (mils/1000 miles), while our abrasions are given in terms of loss in g/1000 km. By calculations using the specific gravity of the tread com-

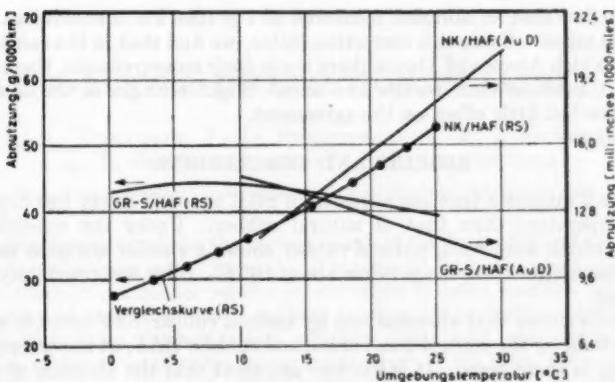


FIG. 2.—Abrasion of SBR compared to natural rubber treads. Data are from various researches. RS = Rubber stichting (comparison curve). NK = Natural rubber. A u. D = Amon and Dannenberg. Abscissa is ambient temperature; ordinate is abrasion (g/1000 km) and (milli inches/1000 miles).

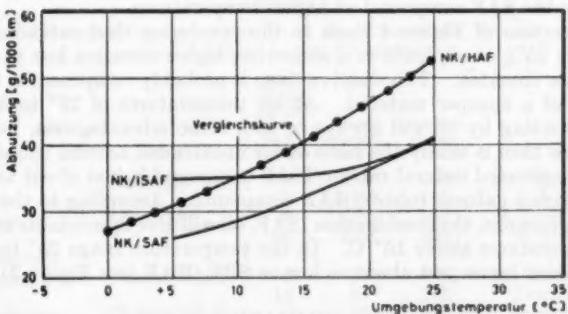


FIG. 3.—Abrasion of natural rubber/HAF compared to natural rubber/SAF and /ISAF. Abscissa is ambient temperature; ordinate is abrasion (g/1000 km).

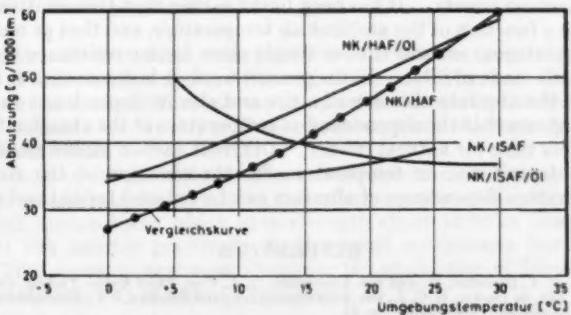


FIG. 4.—Abrasion of natural rubber/HAF compared to natural rubber/HAF/oil treads, and natural rubber ISAF compared to natural rubber/ISAF/oil treads. Coordinates are as in Figure 3.

pound we find that an abrasion measured as 1 g/1000 km is equivalent to 0.32 mils/1000 miles. Using this correction factor, we find that in the range 12° to 32° C, in which Amon and Dannenberg made their measurements, there is good agreement between their results and ours. Slight changes in the conversion factor have but little effect on the agreement.

### RESULTS AND CONCLUSIONS

Figure 2 indicates that the abrasion of SBR is considerably less dependent upon temperature than that of natural rubber. Under the conditions for abrasion which were used, natural rubber shows a smaller abrasion loss than SBR in the temperature range below about 16° C. This was previously shown to be true<sup>1</sup>.

Figure 3 shows that abrasion loss by natural rubber/SAF tread is appreciably less than by the control tread of natural rubber/HAF, at the temperatures prevailing in these tests. It is likewise apparent that the abrasion of natural rubber/ISAF tread is appreciably less dependent on temperature than are the treads made of natural rubber/HAF or /SAF. In this connection, it is shown that the abrasion resistance of the ISAF compound is lower than that of the HAF compounds at lower temperature, whereas it may be every bit as abrasion resistant as the SAF compound at higher temperatures.

Consideration of Figure 4 leads to the conclusion that extending natural rubber with 25% of oil, leads to a somewhat higher abrasion loss as measured for moderate climates. This disadvantage is probably compensated for by the advantage of a cheaper material. At air temperatures of 25° to 30° C and higher, extending by oil will always be in a sense advantageous, because the abrasion loss then is nearly the same as for unextended natural rubbers.

The oil extended natural rubber/ISAF compound is just about as costly as the unextended natural rubber/HAF compound. According to the course of the abrasion graphs, the combination ISAF/oil will give appreciable advantages at air temperatures above 15° C. In the temperature range 25° to 30° C, it shows abrasion losses just about as low as SBR/HAF (see Figure 2).

### SUMMARY

The relative abrasion resistance of tire treads of various types was determined by relatively short but statistically reliable standard tests, with automobiles driven on streets. It has been found earlier that this relative abrasion resistance is a function of the ambient air temperature, and that at medium and lower temperatures, natural rubber treads show better resistance to abrasion than do treads made of SBR. In the present work, it is shown that it is possible to establish the absolute abrasion of a tire and also its dependence on temperature. It appears that the dependence on temperature of the abrasion for SBR is markedly less than for natural rubber. Different carbon blacks show different degrees of dependence on temperature for the abrasion of the compounds. This temperature dependence of abrasion can be reduced for natural rubber by oil extension.

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## FILLER-RUBBER INTERACTION IN LATEX \*

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The principal obstacle to the development of the technology of production of rubber articles from latex (natural and synthetic) up to the present time has been the absence of a rubber reinforcement effect in latex, and the consequent impossibility of obtaining strong rubbers by direct introduction of fillers into latex. Active fillers (carbon black, colloidal silicic acid, zinc oxide, kaolin, etc.) when added to latex either lower the strength of the latex vulcanizates or yield compounds the strength of which falls far short of the values found for compounds made by the usual energy-consuming method of addition of fillers to the dry rubber on rolls or in mixers. In consequence only unfilled stocks are

TABLE I  
COMPARATIVE STRENGTH DATA ON VULCANIZED FILLED  
AND UNFILLED LATEX COMPOUNDS

Latex type	Filler	Filler content per 100 wt. parts mixture	Tensile strength, kg/cm <sup>2</sup>	Relative elongation, %	Authors
Revertex	Bentonite	0	164*	755	A. Van Rossem and J. A. Plaizier <sup>1</sup>
		5	346*	815	
Natural latex	Askangel	0	242*	690	B. Dogadkin and R. Uzina <sup>1</sup>
		30	416*	580	
Butadiene-styrene latex (Igetex S-3)	Channel black	0	16	560	R. Uzina and M. Dostyan <sup>1</sup>
		15	53	210	
Butadiene-styrene (GR-S)	Channel black	0	22	—	Conover**
		45	127	—	

\* These values were obtained in two-dimensional tensile tests by the Flint instrument; they are considerably higher than the usual tensile data obtained by the Schopper dynamometer.

\*\* Conover's review gives numerical data only, without indication of the methods used for preparation or testing of the filled latex compounds.

now made directly from latex, which greatly restricts the range of possible applications of latex technology and its further development.

A number of workers<sup>1</sup> have attempted to solve the problem of reinforcement of rubber in latex. However, as Table I shows, these attempts have not led to the desired results.

The authors of the present paper<sup>2</sup> have succeeded for the first time in determining the conditions for obtaining butadiene-styrene (SKS-30) latex compounds with carbon black which have strength characteristics (in the vulcanized state) not inferior practically to the usual compounds from the same rubber. This opens up new possibilities for the production of filled latex compounds for the solution of technical problems.

\* Reprinted from *Colloid Journal (USSR)* 18, 523-530 (1956); translated from *Kolloidnyi Zhurnal*, Vol. 18, pages 528-535 (1956) by Consultants Bureau, Inc.

*The idea of the investigation.*—In our opinion there are three main reasons for the insufficient reinforcement effect of rubber in latex compounds. First, active fillers (carbon black, zinc oxide, colloidal silicic acid) are distributed in the latex not as primary particles but as more or less large aggregates. The nature of these aggregates varies with the type of filler, its concentration in the latex, and the protective substances used for dispersion<sup>3</sup>.

The first cause of the low strength of latex rubber compounds is the insufficiently fine distribution of the filler in the latex, so that insufficient contact area is developed between the rubber and filler particles.

The second cause is that in a latex mix, even if the dispersed particles are finely and uniformly distributed, they are not deposited simultaneously during formation of the deposit (film), whether by evaporation of water, by coagulation, or by application of the latex mix to a water-absorbing material. The reason for this nonsimultaneity may be a) varying density of the dispersed particles; b) different values of the electrokinetic potential and different rates of its variation by the action of the precipitant (electrolyte) or on change of concentration (in the evaporation of water); c) different surface activity and stability of the protective layers on the particle surfaces; and finally d) varying anisotropic characteristics of the particles, which also influence sedimentation kinetics. Nonsimultaneous deposition of the particles from a latex mix leads to an inhomogeneous, stratified distribution of the film components and hence to low strength in the filled vulcanizates obtained from latex mixes.

The third cause for the absence of a reinforcement effect is the presence of a protective surface coating on the latex globules and carbon particles, which prevents direct contact between the rubber and the filler after removal of the aqueous phase.

The views advanced above are confirmed by direct experiments. If channel black is added to butadiene-styrene latex in the form of a very fine dispersion, then the strength of the vulcanized films containing 40 parts by weight of carbon per 100 parts of rubber is about 12 kg/cm<sup>2</sup>. The same latex mix after milling and vulcanization in a press has a strength of 136 kg/cm<sup>2</sup>. This effect of the milling can be explained on the grounds that milling produces uniform distribution of the components and homogenizes the system to such an extent that direct contact is established between the rubber and the carbon-particle surfaces, and also between the carbon particles without a weakening protective layer between.

This is in full agreement with the theory of rubber reinforcement advanced by one of us<sup>4</sup> and also with the latest data of Garten<sup>5</sup> and Watson<sup>6</sup> on the radical mechanism of rubber-carbon black interaction.

Thus, for the production of filled latex compounds of high strength it is necessary to ensure:

- a) a high degree of dispersion of the fillers and other ingredients added to the latex;
- b) simultaneous precipitation of the particles from the latex mix;
- c) conditions which result in direct contact between the rubber and filler particles, without intermediate layers of protective substances which lower the rubber-filler interaction energy.

It is also evident that protective substances, intermediate layers of which do not diminish the rubber-filler interaction energy and which do not prevent the formation of chemical vulcanization bonds between the latex globules, may

be used without significant detriment to the strength of the latex compounds.

Our experiments were therefore based on the forgoing considerations.

*Composition and methods of preparation of the latex compounds.*—The material for investigation was SKS-30 butadiene-styrene latex containing Nekal (sodium dibutylnaphthalene sulfonate) as emulsifier.

Ukhta channel black was added to the latex in the form of a fine dispersion made in a colloid mill with Leukanol (condensation product of sodium 2-naphthalene sulfonate with formaldehyde) as stabilizer. The vulcanization ingredients were Accelerator 226 (a mixture of Captax sodium salt and triethanolamine), zinc oxide, and sulfur. The zinc oxide and sulfur were dispersed in a ball mill with Leukanol as stabilizer. After addition of all the ingredients, the latex mix was stirred together in a blade mixer, filtered through gauze, and poured into glass cells. The drying was first carried out in air, and the films were then dried in a desiccator over sulfuric acid. The resultant films, ~0.5 mm thick, were vulcanized in a press at 143°C.

*Effect of casein and other protective substances.*—As Figure 1 shows, latex

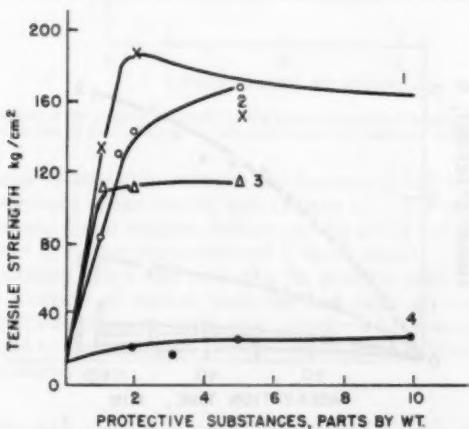


FIG. 1.—Effect of additions on the tensile strength of latex vulcanizates containing 40 parts of channel black by weight: 1) casein; 2) gelatin; 3) sodium alginate; 4) casein without channel black.

films filled with channel black (40 parts by wt.) have a strength of ~25 kg/cm<sup>2</sup> at optimum vulcanization. The strength rises sharply, reaching 190 kg/cm<sup>2</sup>, if casein is added in the form of ammonium caseinate. Gelatin and sodium alginate have a similar effect but to a smaller degree (Figure 1). The maximum reinforcement effect of casein in carbon black compounds is found at a content of ~2% on the rubber. At the same time, addition of casein to latex without carbon black (in various amounts, up to 10% on the rubber) does not produce any significant increase in the strength of vulcanized latex films (Figure 1, Curve 4). Thus, the influence of these substances involves a change in the nature of the interaction between the components of the carbon-latex mix.

Addition of casein results in thickening and at the same time in destabilization of carbon black-latex mixes. This is seen from the microphotographs<sup>8</sup> of the mix before and after addition of casein (Figure 2a, and 2b). The mixture with casein shows large aggregates consisting of rubber and carbon particles

after dilution with water, while in the mixture without casein the disperse phase is uniformly distributed. A similar situation (Figure 2c, and 2d) is found on addition of ammonium caseinate to a dispersion of carbon black alone. The destabilization effect is also seen in the sedimentation kinetics of diluted carbon black-latex mixes.

As Figure 3 shows, the sedimentation rate of the suspended particles becomes about seven times higher on addition of 2% casein (Curve 2) compared with the sedimentation rate in mixes without casein (Curve 1).

The destabilization of the carbon black-latex mixture on addition of casein may be attributed to interaction between casein and the protective substances on the surfaces of the carbon particles and the latex globules (Nekal, Leukanol). We believe that this interaction leads to partial desorption of the protective substances from the surface of the particles in the disperse phase and to formation of coacervates—an effect repeatedly described in papers on destabilization of colloid systems. The carbon particles and latex globules, from which the protective surface layer has been to some extent removed, form structures in which direct contact is established between the carbon and the rubber. Accord-

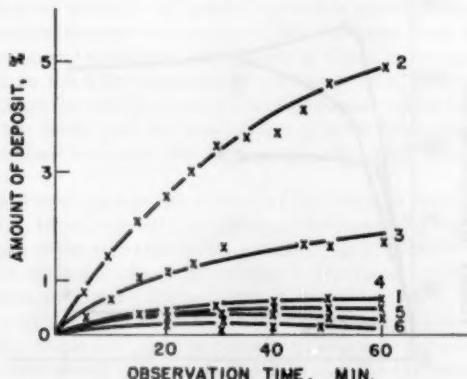


Fig. 3.—Sedimentation kinetics of latex mixes containing 40 parts of channel black by weight: 1) without casein; 2) with casein; 3) casein with 1 wt. part OP-10; 4) casein with 2 wt. parts OP-10; 5) casein with 3 wt. parts OP-10; 6) casein with 4 wt. parts OP-10.

ing to Voyutskii<sup>7</sup> the surface of the globules in SKS-30 latex is not completely covered by a protective layer of emulsifier. This, as was noted above, is one of the conditions for rubber reinforcement. At the same time, the introduction of casein and similar substances, by favoring the formation of secondary structures consisting of rubber globules and carbon black, ensures their simultaneous precipitation in film formation. In other words, another condition for reinforcement is fulfilled—coprecipitation of the components and their uniform distribution in the mix.

The connection between formation of secondary structures in carbon black-latex mixes and vulcanizate strength is confirmed by the following experiments. If varying amounts of stabilizer OP-10 (a reaction product of ethylene oxide and an alkyl phenol) are added to the carbon black-latex mix, followed by casein, then the stability of the mix rises with the OP-10 content (Figure 3). However, this is accompanied by a decrease of vulcanizate strength, and there

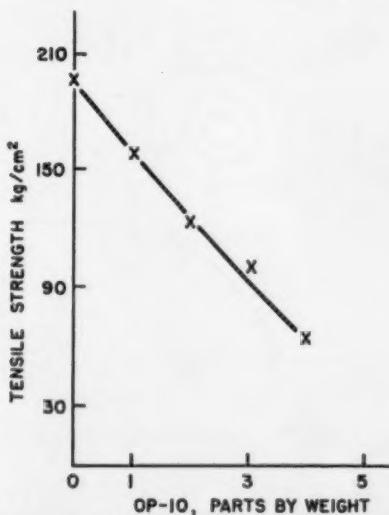


FIG. 4.—Effect of the content of OP-10 on the tensile strength of latex vulcanizates containing 40 parts of channel black and 2 parts of casein by weight.

is an inverse linear relationship between the content of OP-10 in the mixture and the tensile strength of the vulcanizate (Figure 4). The mechanism of the action of various stabilizers requires further careful study for the development of a correct theory of rubber reinforcement in latex mixes.

The destabilization effect can evidently be positive only if it occurs in a well-distributed mixture of carbon particles and latex globules (Figure 5). Only then can redistribution of protective substance between particles of the disperse phase lead to the formation of a fine structure in a filled latex film with high-strength characteristics.

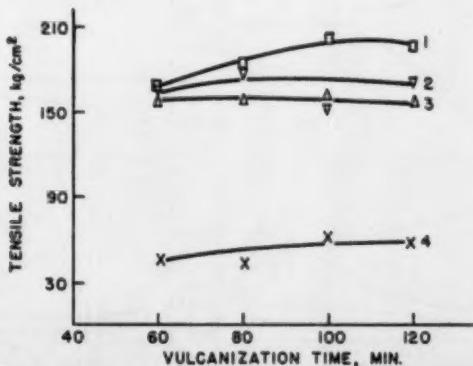


FIG. 5.—Effect of conditions for the production of carbon black dispersions on the tensile strength of vulcanised latex compounds (40 wt. parts of channel black); carbon black dispersed by: 1) colloid mill; 2) ball mill for 48 hours; 3) shaking in a flask for 48 hours; 4) carbon black without mechanical treatment.

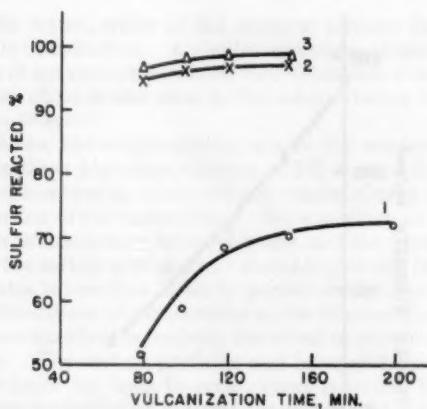


FIG. 6.—Kinetics of sulfur addition in films from carbon black—latex mixes (40 wt. parts of channel black) according to vulcanization conditions: 1) in air; 2) in press; 3) in press, after preliminary milling.

*Effect of vulcanization conditions.*—The existence of protective coatings on the latex globules is a significant obstacle to the formation of chemical vulcanization bonds between them. It is possible to visualize the existence of such layers between the latex globules as would completely prevent the interaction between the vulcanizing agent (sulfur) and rubber. In such cases the vulcanization effect or a due reinforcement effect would not occur. In cases when direct contact takes place in the latex mix between the globules and the filler particles without an intermediate layer of protective substances, the vulcanization effect would be as pronounced as in ordinary mill-mixed stocks. Between these two extremes there are a number of real intermediate states in

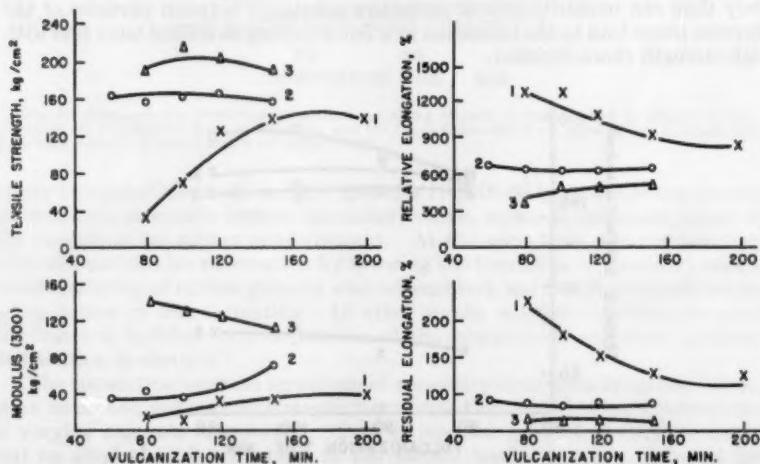


FIG. 7.—Effect of vulcanization conditions on the mechanical properties of latex compounds with 40 wt. parts of channel black; vulcanization: 1) in air; 2) in press; 3) in press, after preliminary milling.

which the vulcanization kinetics and the final degree of development of vulcanization structures depends on the composition of the protective substances, the relative extent of the regions of direct contact between the rubber globules, the thickness of the protective layers, rate of diffusion of sulfur through them, and a number of other factors.

Figure 6 shows the kinetics of sulfur addition in films from a carbon black-latex mix containing 40 wt. parts of channel black, during vulcanization in a thermostat in the air, and in a press, before and after milling. Figure 7 shows the variations of the mechanical properties of the vulcanizates for the same conditions. As was to be expected, during vulcanization in air, the addition of sulfur is slow and in 160 minutes it reaches 70% of the amount of sulfur added. Vulcanization in the press is practically complete in 60 minutes. This difference in the vulcanization kinetics is explained, by the usual factors which determine the differences between press and air vulcanization, and also by the fact that hydraulic pressure during molding increases direct contact between the rubber particles and the vulcanization components. Accordingly, the strength of films vulcanized in air ( $140 \text{ kg/cm}^2$ ) is lower than the strength of

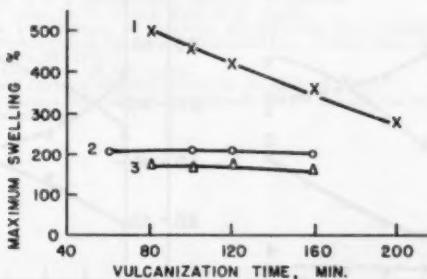


FIG. 8.—Kinetics of swelling of latex mix vulcanizates with 40 wt. parts of channel black in relation to the vulcanization conditions: 1) in air; 2) in press; 3) in press, after preliminary milling.

films vulcanized in the press ( $\sim 170 \text{ kg/cm}^2$ ). The highest strength, as already stated, is found in compounds of the same composition only after milling.

A direct measure of the smaller number of chemical crosslinks in vulcanizates obtained in air is provided by their greater maximum swelling in xylene in comparison with press-vulcanized products (Figure 8). This suggests that the choice of a more active vulcanization system might yield filled latex compounds which would have strength properties after air vulcanization similar to those of press vulcanizates.

*Effect of electrolytic coagulation.*—If a filled latex mixture is coagulated by an electrolyte and the resultant coagulum is vulcanized in a press, the vulcanizate strength is higher than that of latex films obtained by the drying method (see Table II). This strength increase is apparently primarily due to the fact that a part of the protective substances of the latex mix remains in the serum after coagulation. It is also possible that the removal of the charge from part of the disperse phase favors the formation of coagulation structures in which more complete contact is effected between the rubber and filler, and also between the filler particles.

Coagulation of filled latex mixes can be used for the production of granulated rubber mixtures for the manufacture of pressed articles.

TABLE II

PHYSICAL AND MECHANICAL PROPERTIES OF VULCANIZATES WITH 40 WEIGHT PARTS OF GAS CHANNEL BLACK BASED ON LATEX AND ON SKS-30 RUBBER

Properties	Based on SKS-30 latex		Based on SKS-30 rubber compounded on rolls
	Drying method	Electroly- tically coagulated	
Tensile strength, kg/cm <sup>2</sup>	214.2	257.5	297.3
Modulus at 100% elongation, kg/cm <sup>2</sup>	22.2	38.0	12.1
Modulus at 300% elongation, kg/cm <sup>2</sup>	65.5	102.0	52.3
Relative elongation, %	660	572	748
Residual elongation, %	40.4	25.8	30.4
Tearing strength, kg/cm <sup>2</sup>	41.9	43.3	47.1
Shore hardness	84	—	66
Rebound elasticity at 20°, %	35	—	40

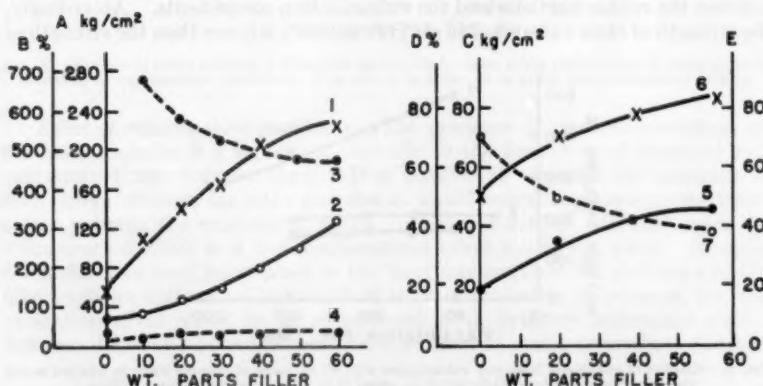


FIG. 9.—Effect of channel black content on the mechanical properties of latex rubber compounds (SKS-30): 1) tensile strength (A); 2) modulus at 300% elongation (B); 3) relative elongation (C); 4) residual elongation (D); 5) tearing strength (E); 6) Shore hardness (F); 7) rebound elasticity at 20° (D).

*Mechanical properties of vulcanizates obtained from filled latex mixes.*—Figure 9 shows variations of the mechanical properties of vulcanizates with the amount of Ukhta channel black. Table II shows data on the mechanical properties of vulcanizates obtained from latex mixes by the drying and coagulation methods, and of vulcanizates of the same composition made by the usual method of compounding on rolls. It is seen that the principal strength properties of these products are similar. There is no doubt, however, that the different nature of vulcanizate structure cannot fail to show itself in a number of properties, such as the modulus, hardness, etc. Nevertheless we believe that our results open up definite possibilities for the production of technically valuable filled vulcanizates directly from latex, and therefore for the development of new technological methods.

#### SUMMARY

Conditions for the production of strong vulcanizates by direct addition of channel black to SKS-30 butadiene-styrene latex have been determined.

Rubber reinforcement by carbon black in latex mixes occurs on addition of such substances as casein, gelatin, and alginic acid to the mixture.

Experimental data are cited to show that the rubber reinforcement effect in the presence of the above substances is due to: a) their destabilizing action and the formation of structures in which the carbon black and rubber particles are in direct contact; b) conditions in which the latex components are precipitated simultaneously (coprecipitation effect).

Electrolytic coagulation of carbon black-latex mixtures results in increased vulcanizate strength.

Vulcanization of filled latex compounds proceeds at a lower rate than that of ordinary rubber compounds of the same composition.

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- 8 Figure 2 in the article was not sufficiently sharp for good reproduction and has been omitted. It consisted of five photomicrographs.

## MODIFICATION OF RUBBER BY REACTION WITH MALEIC ANHYDRIDE \*

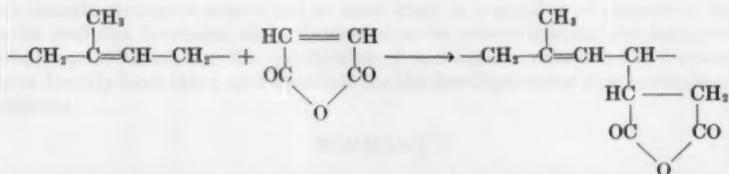
JEAN LEBRAS, CHRISTIAN PINAZZI, AND GÉRARD MILBERT

The reaction between maleic anhydride and rubber has been studied in solution<sup>1</sup>, by milling<sup>2</sup> and by heating in the solid phase<sup>3</sup>. However, as is most often the case with chemical derivatives of the rubber hydrocarbon, the operating conditions that were employed only yielded products exhibiting considerable impairment to the physical properties characteristic of rubber (especially its high elasticity) as a result of secondary reactions of scission, cyclization and crosslinking. It has subsequently been shown that it is possible, under certain conditions, to minimize these injurious effects, both in the case of the reaction in solution between natural rubber and maleic N-methylimide<sup>4</sup> and in that of the reaction by milling between synthetic olefinic elastomers and maleic anhydride<sup>5</sup>.

Inspired by these studies, we have undertaken to re-examine, on more precise chemical bases, the reaction between the rubber hydrocarbon and maleic anhydride.

The reaction is effected in a sealed tube, in an atmosphere of oxygen-free nitrogen under reduced pressure, in toluene solution, and in the presence of antioxidants (2,6-di-*tert*-butyl-4-methylphenol and 6-phenyl-2,2,4-trimethyl-1,2-dihydroquinoline) for the purpose of minimizing the scission and crosslinking reactions. The ratio of maleic anhydride to rubber is varied from 25 to 400 per cent by weight. The reaction is carried out at 180°, and the time of reaction is varied from 30 to 180 minutes. The product of the reaction is precipitated and washed with acetone or ethanol, then redissolved in benzene and reprecipitated until all the free anhydride and the antioxidants are eliminated, and finally dried under vacuum until all traces of solvent have disappeared.

The influence of the antioxidants is clearly revealed by gel rubber measurements, which give an indication of the crosslinking condition of the product. It has been found, for example, according to whether antioxidants are used or not a reaction time of 120 minutes yields respective gel rubber ratios of 1.2 and 4.2 in the case of an initial ratio of 25 per cent of anhydride (combined ratio about 2 per cent) and of 2.8 and 26 in the case of an initial ratio of 400% of anhydride (combined ratio about 12 per cent). It may be concluded that the product obtained exhibits practically no crosslinking, and granting (in accordance with previous studies<sup>6</sup>) that it is the CH<sub>2</sub> in the 4-position which is the most probable reactant, the linear molecule of the product may be assumed to correspond to the formula:



\* Translated by D. M. Beach from *Comptes Rendus des Séances de l'Académie des Sciences*, Vol. 246, pages 1214-1217 (1958).

The quantities of combined anhydride are determined by direct micro-analysis of the oxygen. From the ratio of oxygen found in the rubber control sample (which has undergone the same treatments as the anhydro succinic rubber, but in the absence of anhydride) and from the theoretical formula given above, it can be calculated from the results of the analysis that products A and B shown in the Table I correspond, respectively, to ratios of 5.5 and 22 per cent of combined anhydride, or 4 and 20 anhydro succinic groups per 100 isoprene linkages.

The special properties of such an anhydro succinic rubber were verified by obtaining the corresponding carboxylic derivative, as well as its benzylic ester and its anilide. It is also of interest to note the changes in solubility: in con-

TABLE I

	% Anhydride added	C %	H %	O %
Pale crepe, control sample	0	88.4	11.5	1.2
Product A	50	83.5	11.7	4.0
Product B	400	77.1	10.1	12.0

trast to the rubber hydrocarbon, its anhydro succinic derivative B is completely soluble in methyl ethyl ketone or butyl acetate and is insoluble in hexane. In addition, this derivative can be vulcanized (Table II) by the simple action of a metallic oxide, such as the oxide of zinc or magnesium, as well as by diols, diamines or diisocyanates, whereas, under the same conditions, unmodified rubber gives no sign of vulcanization.

The yield of the reaction, expressed in the ratio of combined anhydride to the anhydride employed, is low. But we only intended here to obtain an anhydro succinic rubber with a high combined anhydride content and with the least possible crosslinking, in order to be able to establish the fact of the reaction as

TABLE II  
MECHANICAL PROPERTIES OF SOME VULCANIZATES

% Combined anhydride	Vulcanizing agent	Modulus at 300%, kg/cm <sup>2</sup>	Tensile at break, kg/cm <sup>2</sup>	Elong. at break, %
Ordinary rubber	0	8 + accelerator	40	200
Rubber control sample	0	8 + accelerator	30	60
Anhydro succinic rubbers	5	8 + accelerator	160	180
Anhydro succinic rubbers	5	ZnO	83	400
Anhydro succinic rubbers	24	MgO	140	640

shown by analytical data and to show the modifications in properties emanating therefrom.

On a more practical scale, we also conducted the reaction in internal mixers, in a current of nitrogen, limiting ourselves to small quantities of combined anhydride (from 1 to 4 per cent) sufficient to produce substantial changes in the properties of the elastomer. Such an anhydro succinic rubber can be vulcanized by the agents indicated above, and the vulcanizates display special technological characteristics which will be described in another publication.

These experiments have thus shown that it is possible to fix onto rubber, without impairing its high elasticity, reactive groups which give it a degree of polarity capable of imparting new characteristics to the vulcanizates.

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- <sup>6</sup> See, for example: Gee, G., *Trans. Inst. Rubber Ind.* 25, 98 (1949).

## A UNI-ROTOR MIXER FOR RUBBERS AND PLASTICS \*

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Internal mixers for rubbers and plastics almost universally possess horizontal twin rotors and often a ram for directing material between the rotors. This mixing principle has some disadvantages from both the engineering and operational aspects, for example, the uneven torque during mixing, the difficulty of adequately preventing escape of material, inter-charge contamination at the shaft-sealing glands. An alternative mixing principle which has certain attractive features is a single vertical rotor concentric in a chamber, rotor and chamber wall being designed to impart both lateral and downward motion to the material to achieve mixing with no losses from the open top of the chamber.

It was convenient to test such uni-rotor mixing on a laboratory-scale machine in the first instance. Further, the laboratory mixer might fulfil a need since limitations of reduction in size, temperature control, loss of material and

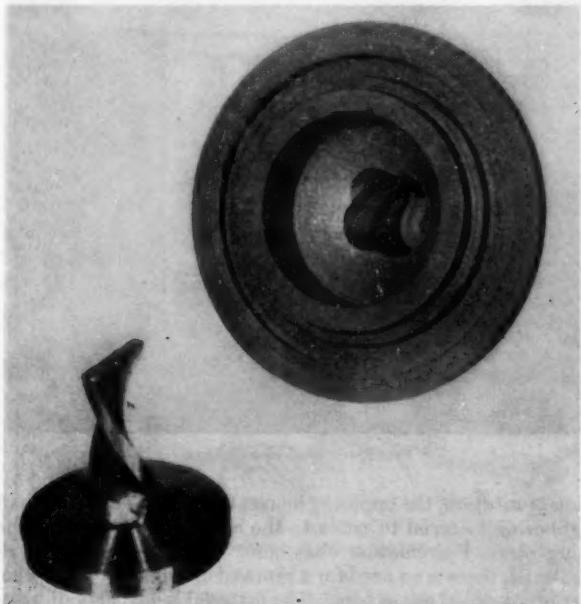


FIG. 1.—Rotor and chamber components.

\* Reprinted from the *Rubber and Plastics Age*, Vol. 38, No. 11, pages 982-983, November 1957. Also published in *Rubber Age* (N. Y.), Vol. 82, pages 296-299, November 1957.

advent of impurities, and the presence of atmospheric gases make small-scale versions of two-rotor mixers inadequate for precise laboratory experimentation. The mixer described below has been in regular use in the BRPRA laboratories for several years and has come to be regarded as routine equipment for small-scale mixing operations.

#### DESCRIPTION OF MIXER

The rubber or plastic and compounding ingredients are contained in a generally cylindrical or slightly conical chamber and are mixed by the rotation of a twisted blade, Figure 1, inserted concentrically in the chamber. With the cor-

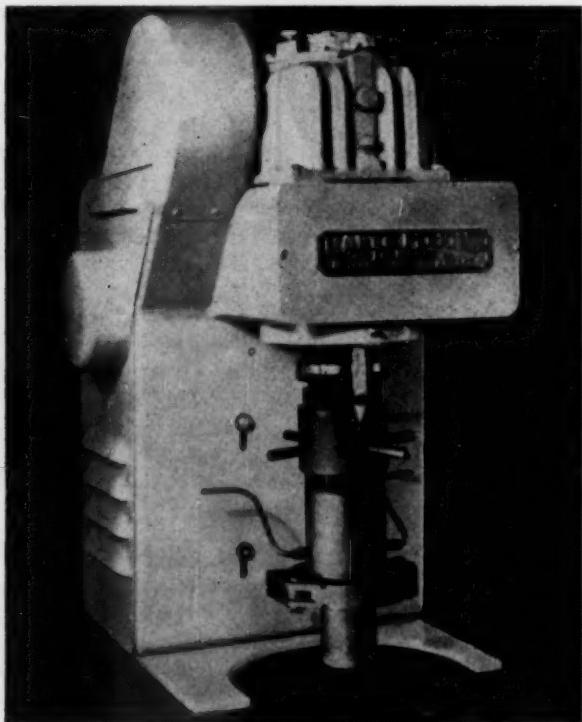


FIG. 2.—General view of mixer.

rect direction of rotation, the opposing helices of the rotor and the chamber wall induce neighboring material to move to the closed end of the chamber, with a compensating upward circulation elsewhere. Consequent on the downward urging of material, there is no need for a ram and no tendency for escape although the chamber is not closed at the top. The material is also periodically squeezed between the rotor edges and the groove ridges in the chamber, an even number of grooves giving equal thrusts on both edges of the rotor. The resultant complex motion has been found to produce efficient mixing.

The rest of the apparatus, shown in Figures 2 and 3, rigidly holds the chamber concentric with the rotor at a selected depth of insertion and provides drive to the rotor. The shaft, Sh, can be rotated at 11 to 90 rpm by a 1-hp 1440 rpm motor acting through an infinitely-variable speed v-belt drive and a worm-

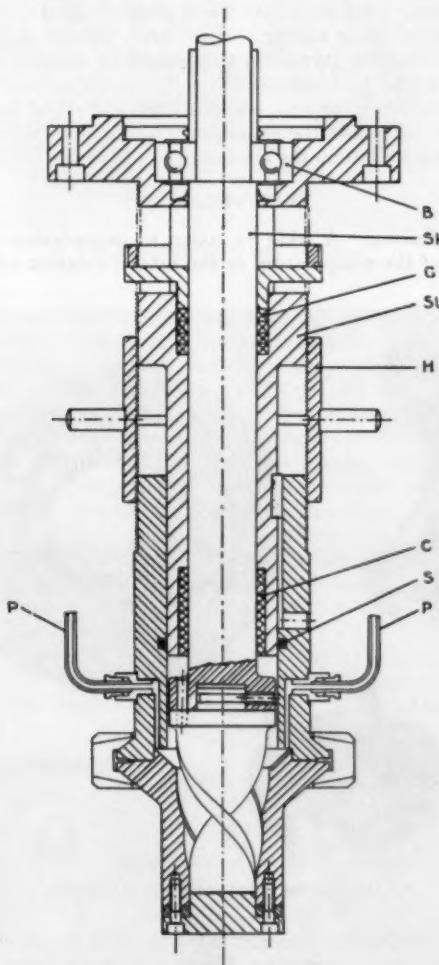


FIG. 3.—Sectional diagram of mixing-head assembly.

reduction gear. The shaft is supported within its sleeve, Sl, by a ball-bearing race, B, and a carbon dry-sleeve bearing, C. A gland ring and packing, G, together with "O" ring seal, S, makes vacuum-tight the annular space between shaft and sleeve so that mixings can if necessary be carried out under inert

gases, or at pressures from a few mm mercury to several atmospheres by appropriate connections to the gas inlet and outlet ports, P. Rotation of a capstan-head, H, which is calibrated by a helical scale, lowers or raises the chamber to a selected depth of insertion of the rotor.

The normal operating procedure is to wind the capstan-head to give the maximum retraction of the rotor into the shaft sleeve and attach the chamber containing the materials for mixing. If required, the gas in the mixer is then changed and the chamber immersed to a depth of several inches below the surface of liquid in a portable thermostatically-controlled bath. The capstan-head then raises the chamber with occasional revolution of the rotor until the latter bears on the bottom of the chamber. Mixing is carried out for a period controlled by a time switch on the electrical supply to the motor.

#### PERFORMANCE

*Degradation efficiency.*—A wide variation in degradation efficiency is obtained by choice of the temperature or the rate of rotation of the blade. An

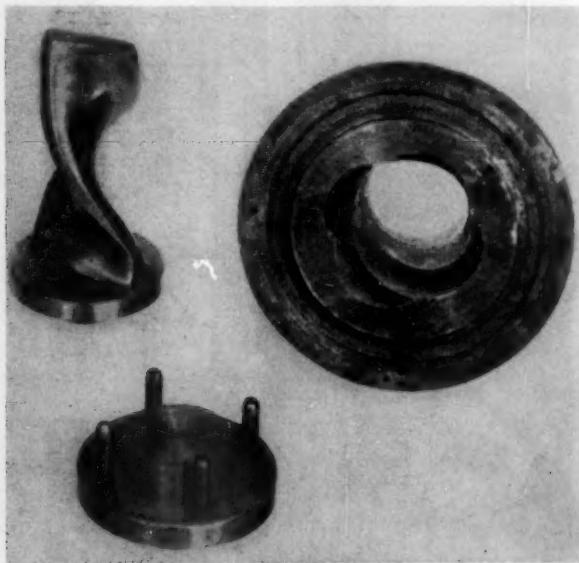


FIG. 4.—Tapering rotor and chamber components.

alternative means of altering efficiency is the use of a chamber tapering to the closed end and a complementary rotor, Figure 4, to give various clearances when the rotor is inserted to varying depths. Spacers provide predetermined clearances when the rotor is lowered until bearing on the bottom of the chamber.

*Temperature control.*—An important distinction from conventional small mixers is temperature control of the masticating material within relatively narrow limits, for example within 5° C and 2° C of the temperature of the thermostating liquid at 20° C and 140° C, respectively, for normal rates of break-

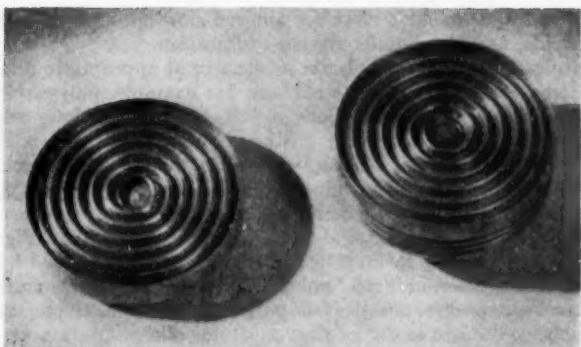


FIG. 5.—Spiral-screwed rotor and stator.

down of natural rubber. It is, however, often convenient in simple compounding to dispense with immersion in a thermostatted liquid.

*Variation of charge.*—Similar efficiencies of compounding are obtained with a variation of charge of greater than one to five in any selected chamber. The chambers of Figures 1 and 4 take charges of 2–10 g and 10–50 g, respectively.

*Mixing of rubber and additives.*—Under normal conditions of mastication in air during which rubber is softened and becomes tacky, vulcanizing ingredients added initially with unmasticated smoked sheet are incorporated within a few minutes' mastication. The chamber after mastication appears visibly as clean as it was originally and no batch-to-batch transfer of small amounts of material has been detected. The homogeneity of compounded gum stocks was tested by vulcanizing and swelling samples from different parts of the same sheet in *n*-decane. No inhomogeneity was detectable within the  $\pm 1$  per cent accuracy of the swelling measurement.

Carbon black in amounts at least up to tire-tread stocks are also satisfactorily incorporated after a few minutes' mastication of the materials added in one batch. Homogeneity tested for as above was within experimental error. A

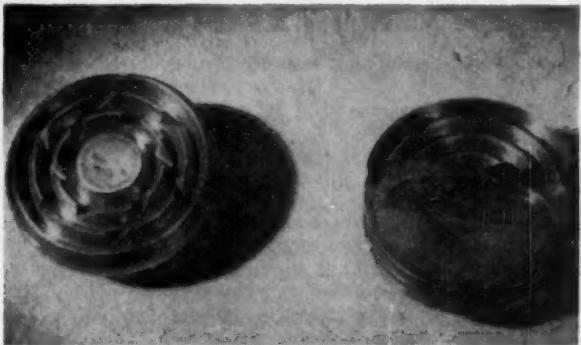


FIG. 6.—Plough-shaped rotor and stator.

hole drilled in the detachable chamber allowed slow addition of carbon black and other solids, and also liquids, during mastication.

*Mixing of plastics.*—Thermoplastic substances at appropriate temperatures have been treated in the mixer as rubbers, for example, polyethylene, polystyrene, and polymethyl methacrylate at 120, 130, and 190° C, respectively. As an illustration of homogeneous mixing, polystyrene mixed with a small amount of a dye gave optical densities of samples taken from different parts of the mass within 1 per cent of the value calculated for the amount of dye added.

*Other mastication fitments.*—Other rotor and chamber designs have been of value for special purposes. A spiral-scrolled rotor and chamber, Figure 5, has been employed extensively in investigations of degradation caused by shearing forces and mastication-induced polymerization. A plough-shaped rotor, Figure 6, has been used for mastication-polymerization and the mixing of very stiff materials.

### CONCLUSIONS

The most pertinent advantages of this one-rotor machine as compared with two-rotor laboratory mixers may be summarized briefly as follows:

- (1) Simplicity and cheapness of construction and robustness. Energy available of up to 1-hp per g material. Even torque characteristics. No contact of masticating materials with seals or glands.
- (2) Ease of operation and economy of batch size. No ram required nor feed for additives.
- (3) A five-fold variability of charge without impairing mixing efficiency. Insignificant charge losses or batch-to-batch retention.
- (4) Rigid control over temperature and gases present.

### ACKNOWLEDGMENT

We are pleased to record our thanks to members of the staff of Baker-Perkins Ltd., Peterborough, for their encouragement and assistance. Baker-Perkins Ltd. built the machine and are currently collaborating under licence in the development of laboratory and larger mixers employing the uni-rotor principle.

We also wish to thank Dr. Bateman and the Board of the British Rubber Producers' Research Association for permission to publish this article.

# A SIMPLE EXTENSOMETER FOR TENSILE TESTING OF POLYMERS \*

A. E. EAGLES AND A. R. PAYNE

RESEARCH ASSOCIATION OF BRITISH RUBBER MANUFACTURERS  
SHAWBURY, SHREWSBURY, SHROPSHIRE, ENGLAND

A description has recently been published of an improved dynamometer for tensile testing of rubberlike polymers, making use of modern electrical methods of measuring and recording forces<sup>1,2</sup>. An account of this device and its applications in rubber testing was presented to the London Section of the Institution of the Rubber Industry in January, 1957<sup>3</sup>.

As a further step in the improvement of tensile testing, an extension-measuring device has now been constructed which enables the percentage elongation between the benchmarks of a dumbbell testpiece to be continually measured and recorded.

## DESCRIPTION

Several devices using various principles have been developed for the measurement of elongation of dumbbells. Typical of these are the Imperial Chemical Industries, Ltd., weightless lever system operating cams<sup>4</sup>; a method using optical periscopes manually adjusted to follow the reference lines on the dumbbell<sup>5</sup>; and the servomechanism of Klute, Penther, and McKee<sup>6</sup> using lightly clamped cantilever springs. In routine testing, however, the method using a ruler held adjacent to the test specimen is still widely employed.

In the B.S. 903 tensile method two parallel reference lines are marked on the narrow part of the testpiece; these are placed symmetrically about the center and are generally one inch apart. The elongation is usually measured by following the travel of the reference lines by means of a suitably graduated ruler, but the method is not entirely satisfactory because:

- (1) Two marks which can become widely separated have to be observed at the same time;
- (2) The ruler must be a finite distance from the specimen, so that errors due to parallax are difficult to avoid;
- (3) The reference lines widen at high elongation, making it difficult to determine their true position;
- (4) The method can only be used easily at room temperature;
- (5) The result depends on the skill of the operator.

These considerations, together with those of fatigue to operators and the desirability of providing an autographic method, encouraged the design of a simple automatic device which would be applicable to the electronic dynamometer. In this design care had to be exercised to avoid abstracting an appreciable amount of energy for operating the mechanical device by the specimen and

\* Reprinted from *The Rubber and Plastics Age*, Vol. 38, No. 9, pages 811-813, September 1957.

to avoid the creation of areas of stress concentration sufficient to affect the validity of the elongations recorded. It is considered that the apparatus described fulfils these requirements and can be utilized for measurements over a

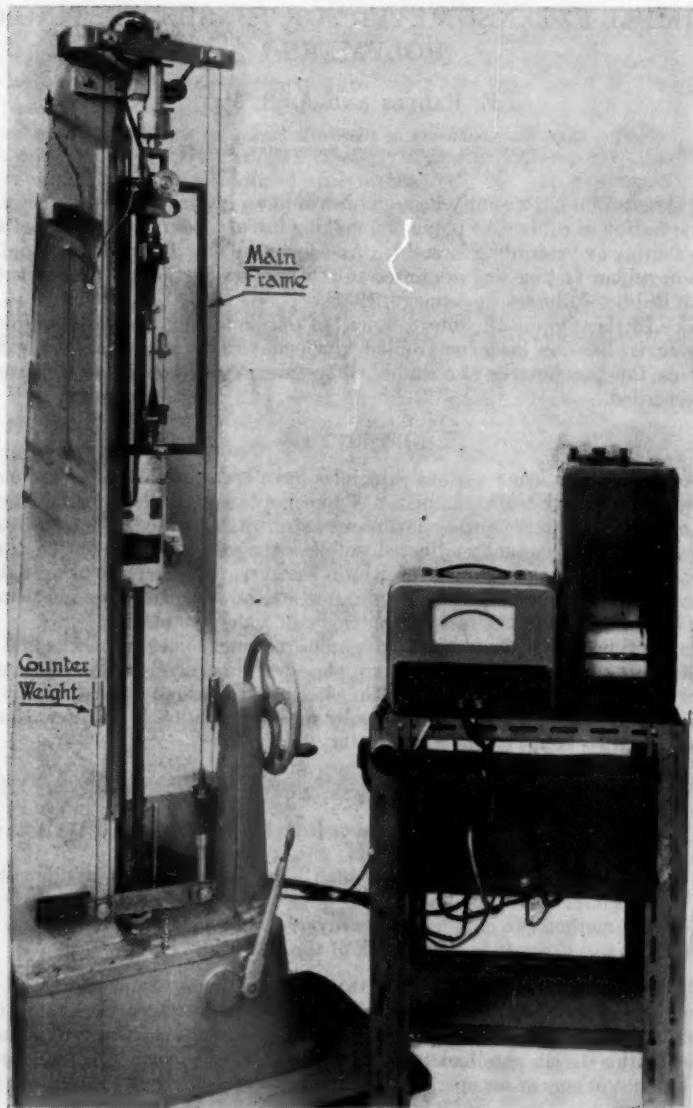


Fig. 1.—Photograph of extensometer.

range of temperatures. A photograph of the complete extensometer is shown in Figure 1.

In order to ensure that the energy abstracted from the rubber is an absolute minimum, it was necessary to make the apparatus as nearly as possible inertialess and frictionless, and such as to impose practically no load on the test-

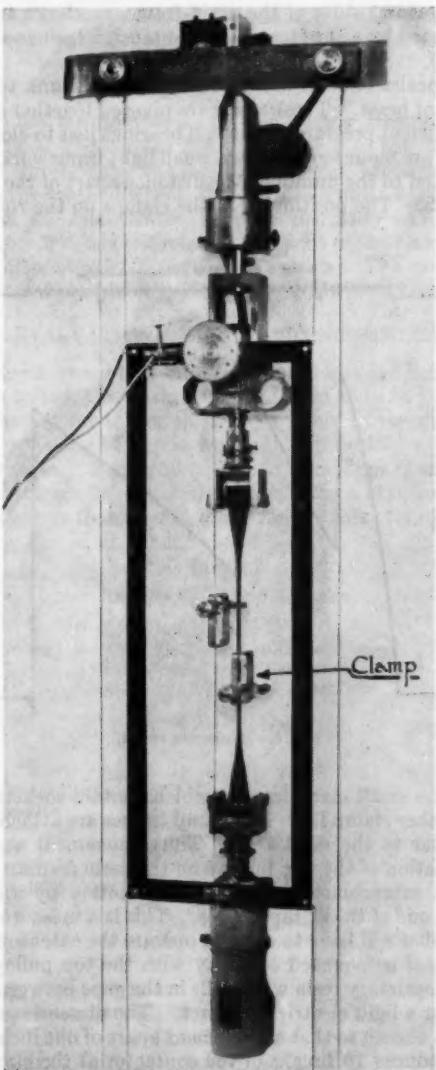


FIG. 2.—Measuring assembly.

piece. For this reason the measuring assembly and the main frame are supported by a symmetrical pulley system incorporating tensioning springs and counterbalance weights. The pulleys are mounted on precision miniature ball races with low friction, and the balance is such that the frame moves under an additional load of about 3 grams.

Two further pulleys are mounted on precision ball races centrally on the short (top and bottom) sides of the main frame, as shown in Figure 2. The clamps are supported by a cord incorporating tension springs and passing round these pulleys.

The clamps consist of two miniature ball bearings sunk to half their diameter in two strips of brass. These strips are pivoted together and spring loaded so as to apply sufficient pressure on the ball bearings just to close them together. Two such clamps are mounted each on a small light framework so that when the clamps are attached to the dumbbell the distance apart of the points of contact is exactly one inch. The positioning of the clamps on the rubber is controlled

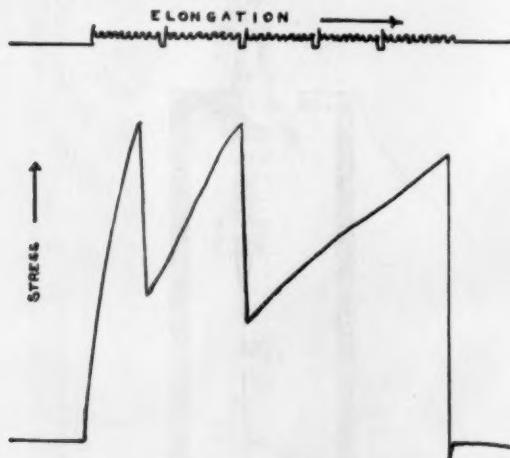


FIG. 3.—Illustrative record.

by two lugs on the small clampframes, which contain sockets into which pins attached to the other clamp fit. The clamp frames are attached one to the left cord and the other to the right cord. Thus, movement apart of the clamp frames causes rotation of the two pulleys on the main frame.

The complete extensometer can be set in motion by applying a load of about 4 grams to one of the clamp frames. This is a measure of the maximum force that the rubber will have to exert to operate the extensometer.

A toothed wheel is mounted coaxially with the top pulley. This wheel is embedded in a proprietary resin which fills in the gaps between teeth, providing a smooth track for a light electrical contact. The dimensions of the wheel and pulleys have been chosen so that a movement apart of one inch of the clamps on the dumbbell produces 10 breaks of the contactor at the circumference of the toothed wheel.

The makes and breaks of the contactor with the grounded toothed wheel operate the relay of the event pen of the recorder. In this manner a record of each 0.1 inch increase in elongation is placed on the chart relative to the corresponding stress signal obtained from the dynamometer, as illustrated in Figure 3; for the stress measurements use has been made of the multirange amplification which enables a more accurate determination of the stress, particularly at low elongations, to be made at each 10 per cent elongation. A device is incorporated to give an enlarged mark at every 100 per cent elongation.

#### MODE OF OPERATION

The operator fits the dumbbell into the testing machine, which uses the Gavin type of grip. The clamps are then clipped to the dumbbell, ensuring that the lugs are correctly positioned. As extension proceeds the clamps move apart and rotate the toothed wheel; there is also a downward movement of the upper clamp, and the main frame, which is delicately balanced, follows this movement. Figure 2 shows the relative positions of the clamps and the lowering of the frame after about 200 per cent extension. The system is sufficiently robust to withstand the sudden rupture at break without damage.

#### EVALUATION OF THE EXTENSOMETER

*Rubbers tested.*—Five rubbers differing in hardness and hence in stress-strain relationship were tested; the hardness ranged from 36 to 83 B.S. degrees.

After conditioning for a minimum of 24 hours in the dark at  $20 \pm 2^\circ C$ , dumbbells were cut along the grain from random positions in the cured slabs, using a Schopper press. The dumbbells used were Type C and Type D<sup>8</sup>. The thickness of the dumbbells was determined using a standard thickness gage and the dumbbells were then dusted with French chalk; those for the pendulum

TABLE I  
RELATIVE TIMES REQUIRED

P = Pendulum tester  
 R = Electronic and ruler  
 E = Electronic and extensometer  
 Times in minutes for 50 dumbbells

##### Type C Dumbbells

	P	R	E
Test	112	84	80
Work out results	110	60	57
Check results	59	31	32
	281	175	169
% of Pendulum test	100	62	60

##### Type D Dumbbells

	P	R	E
Test	118	88	87
Work out results	97	57	50
Check results	54	32	34
	269	177	171
% of Pendulum test	100	66	63

type tensile test machine and for the tests using the electronic tester with ruler elongation measurement were marked with benchmarks at the required gage length; no benchmarks were required for the new extensometer.

*Test procedure.*—Since the sole purpose of this investigation was to compare the performance of the new extensometer with the conventional ruler method, every effort was made to eliminate the effect of personal bias, to maintain identical testing conditions, and to minimize differences in specimen preparation. The test specimens were prepared by the same person, who performed all the tensile tests. These were carried out at a temperature of  $20 \pm 2^\circ\text{C}$  with machines giving rates of traverse of the driven grip of  $20 \pm 2$  inches per minute.

Ten specimens of each shape from each mix were tested by three methods: (1) conventional pendulum tester with ruler elongation measurements; (2) electronic force measurement with ruler elongation measurement; (3) electronic force measurement with new extensometer.

The values of the tensile strength, elongation at break, and stress at 100 per cent, 200 per cent, 300 per cent, 500 per cent and 700 per cent elongation were determined. The coefficient of variation was evaluated from the results obtained. In addition, the times required to carry out the test, work out the results and check the results, were noted (Table I).

#### DISCUSSION

*Breaking elongation.*—The criterion for the success of the extensometer is that there should be no significant decrease in the elongation or stress recorded at break. An examination of the test results shows that in all mixes for either dumbbell there is no statistically significant difference between the results either for means or medians.

In confirmation of the results found from the elongation measurements, an examination of the position of break from the dumbbells tested by the new extensometer was carried out. This showed there was no tendency for breaks to take place other than in a random manner.

*Tensile strength.*—There is no statistically significant difference between the results yielded by the different methods.

*Stress at given elongation.*—For softer rubbers at low elongations there is a significant difference between the results of the pendulum method and those of both the electronic methods, those given by the electronic methods being markedly higher wherever the stress is less than about 300 psi. This is attributed to the greater inertia and friction in the pendulum dynamometer, as was found in a previous comparison<sup>9</sup>. There is usually no significant difference between the results obtained with the automatic extensometer and by the use of a ruler with the electronic testing machine. The coefficient of variation is markedly lower for the extensometer method, which demonstrates that stress at a given elongation can be more accurately determined at low elongations by this method than by the conventional ruler method.

For the higher stresses the results given by the three methods do not differ significantly.

*Time for testing.*—As will be seen from the records of time taken in carrying out the tests (Table I), there is a considerable saving. This is achieved partly in the actual testing, but mainly in the time required to work out and check the results.

## CONCLUSIONS

The prototype extensometer, which has now been in constant use for over a year, gives satisfactory results which compare favorably with those of the conventional method.

The use of this extensometer, which is a simple mechanical device, robust and reliable in operation, removes the last obstacle from autographic recording of tests using dumbbell specimens, thus permitting a considerable increase in speed of tensile testing.

## ACKNOWLEDGMENT

This work is based on Research Memorandum R405 issued by the Research Association of British Rubber Manufacturers.

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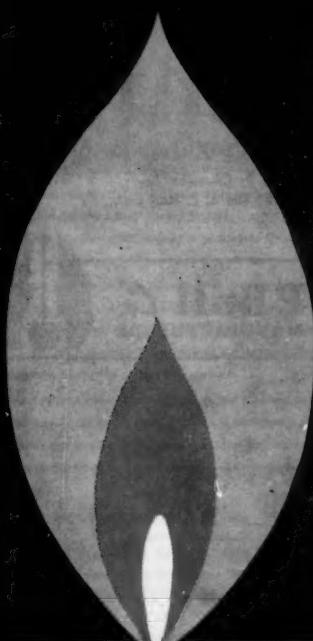
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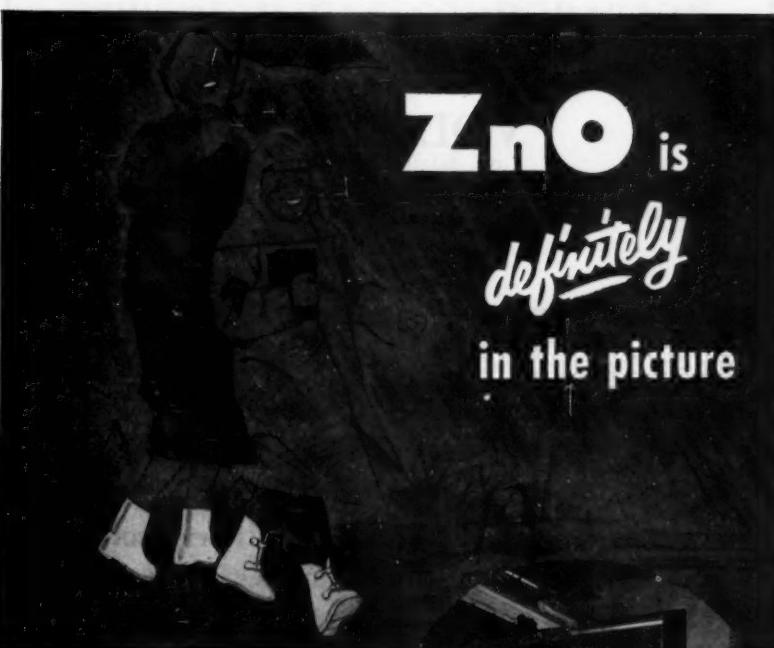
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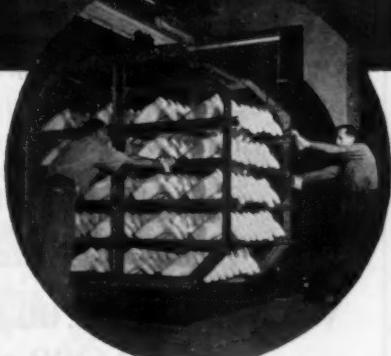
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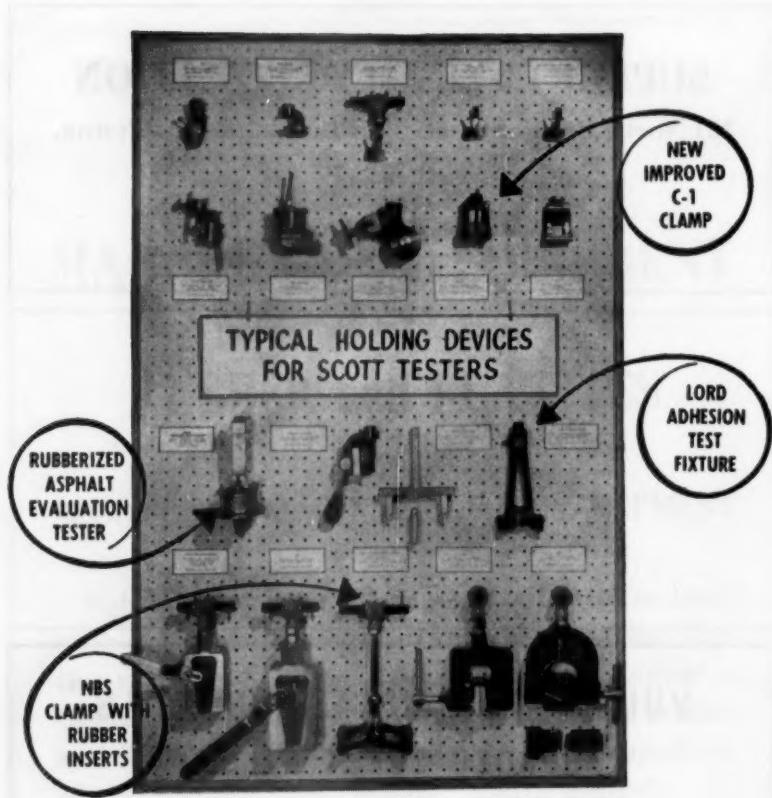
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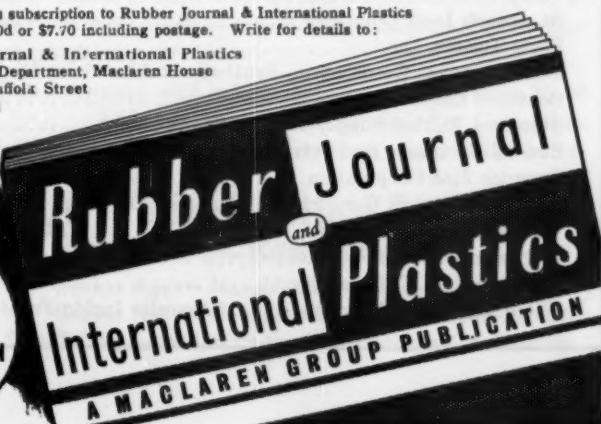
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